Biomass-Based Energy Production

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Renewable Resources: Nature and Availability

We can express an equation whereby the Earth's capacity (EC) is defined as the product of world population *P, the economic activity of an* individual *C and a conversion factor between activity and environmental burden B:*

$EC = P \times C \times B.$

We need to find new ways of generating the chemicals, energy and materials as well as food that a growing world population (increasing P) and growing individual expectations (increasing C) needs, while limiting environmental damage B.

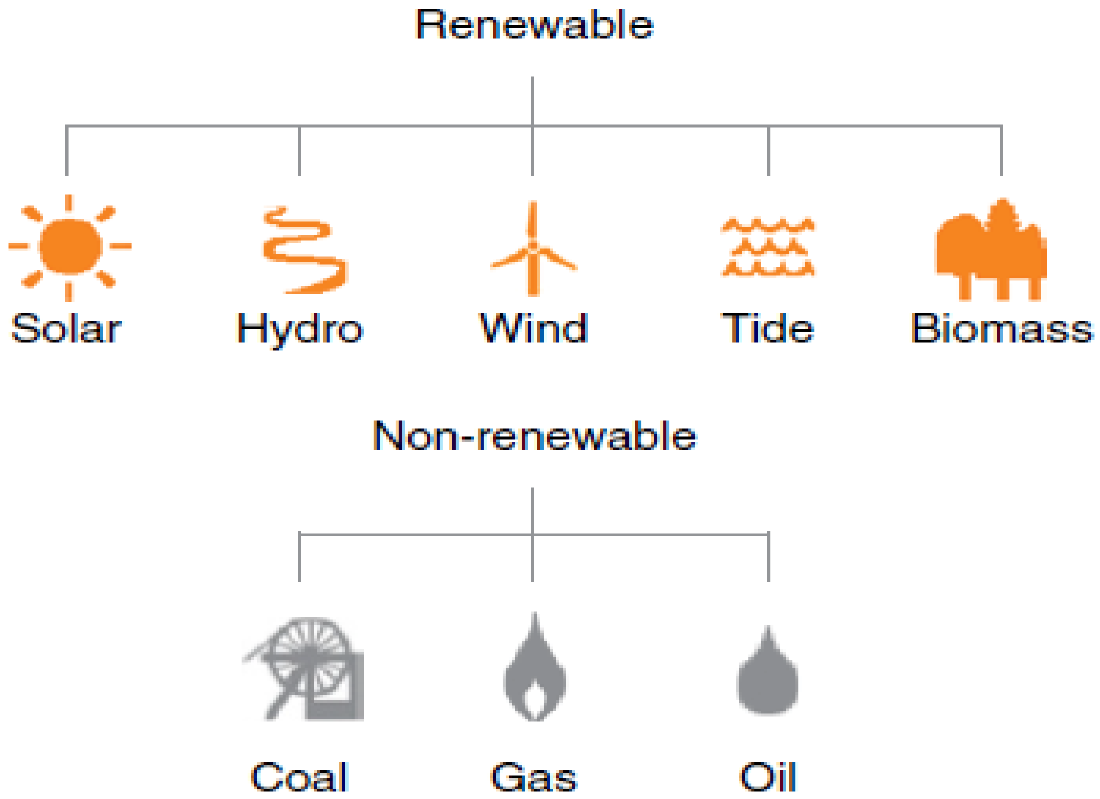
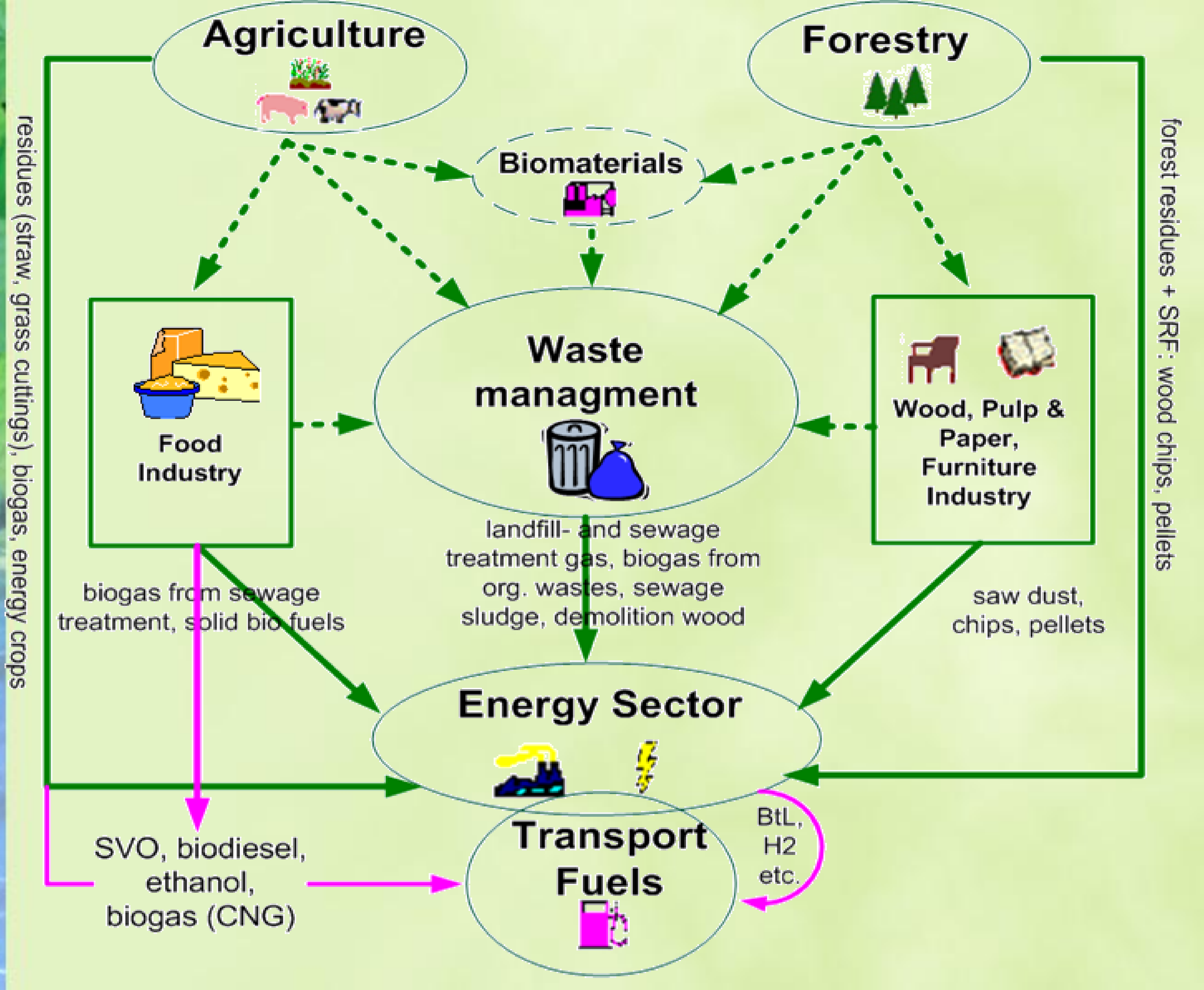
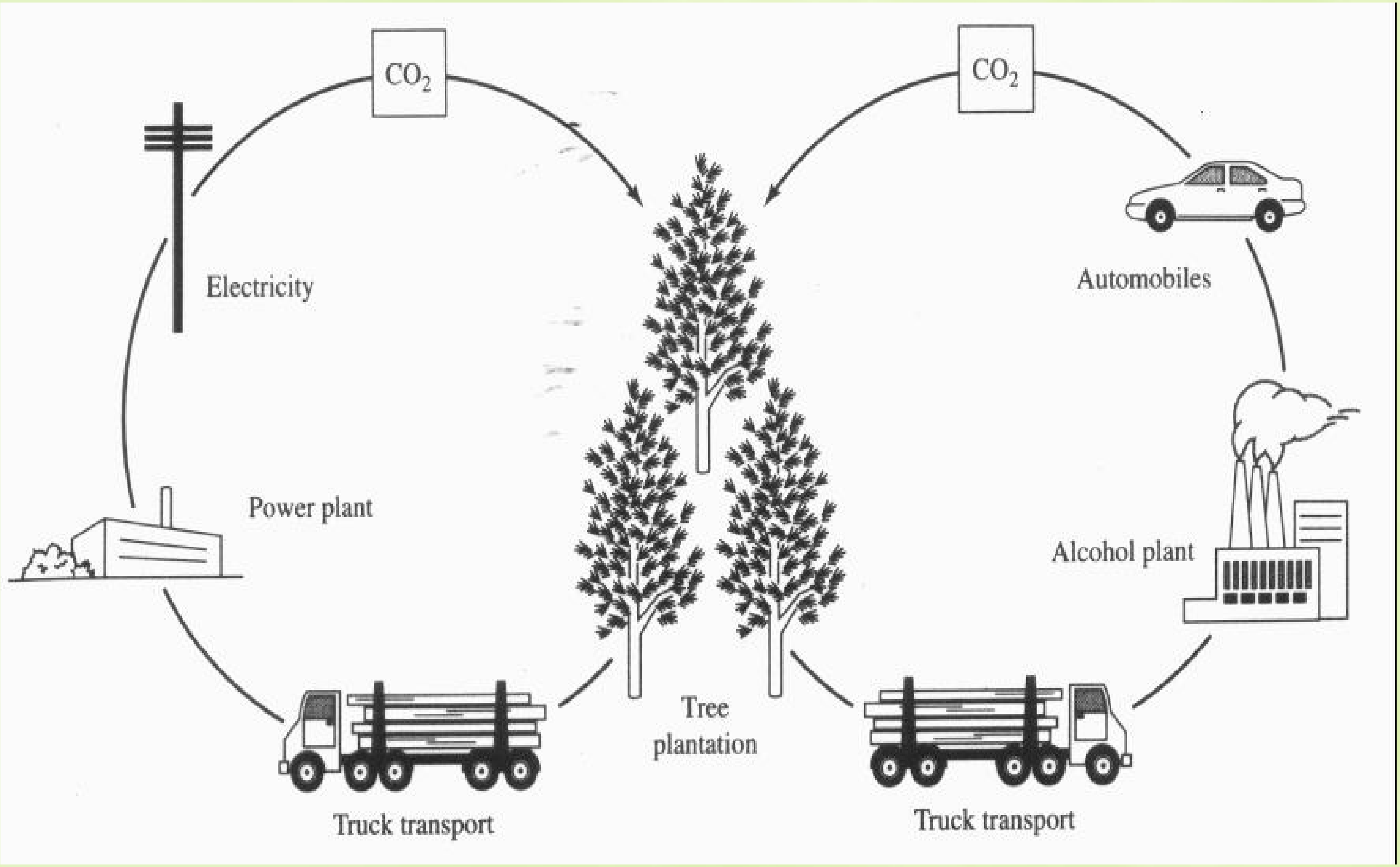


Figure 1.1 *Different types of renewable and non-renewable resources.*

biomass can be used to produce not only energy but also chemicals and materials

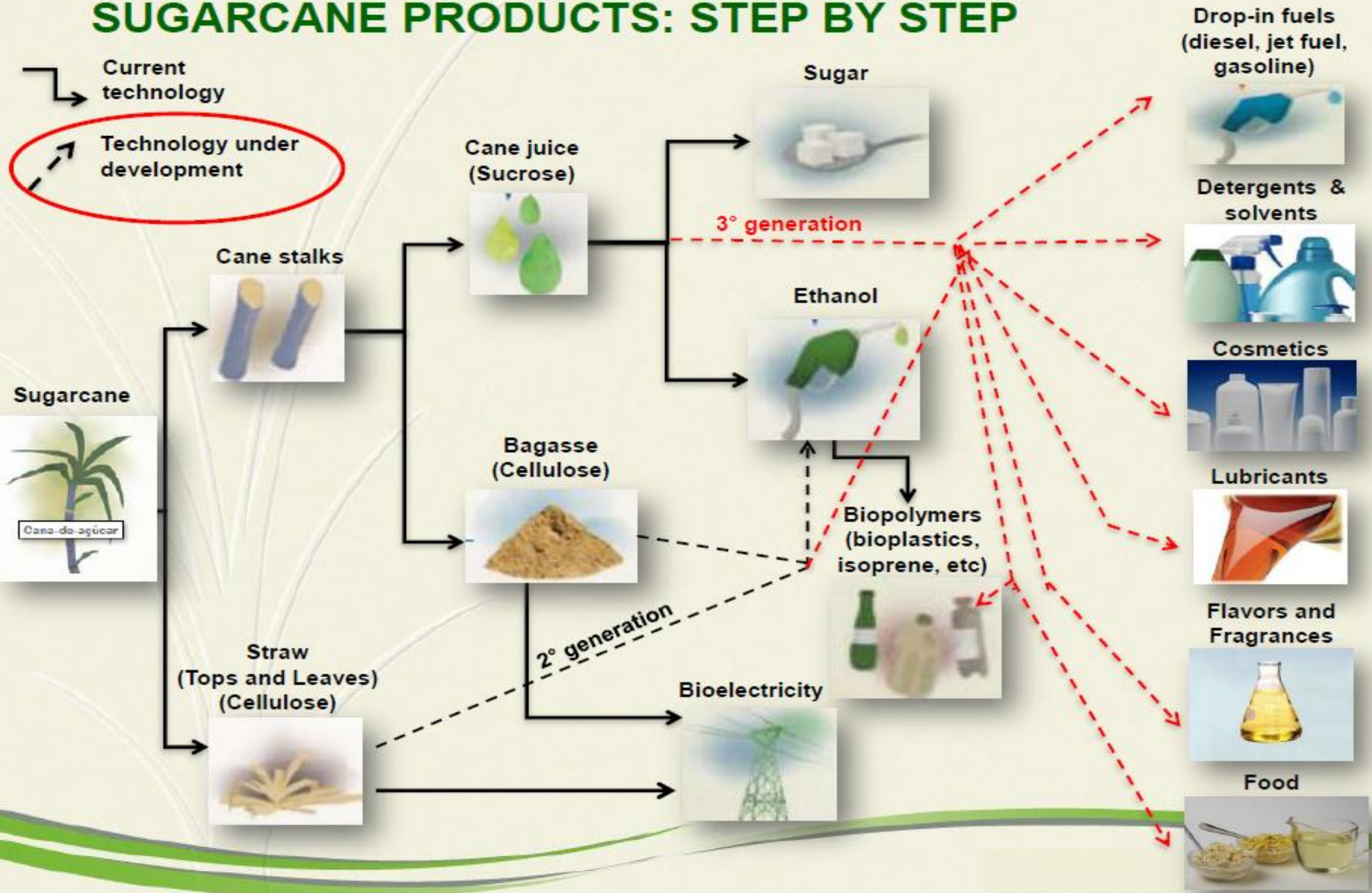
Biomass is a renewable energy source comprising a wide range of biological materials that can be used as fuels and as precursors for the production of other industrial chemicals. Energy generated from biomass is usually referred to as Bioenergy. In general, biomass-derived fuels may be solids (e.g. chips, pellets), liquids (e.g. ethanol, biodiesel), or gases (e.g. biogas, hydrogen). They can be classified based on the processes used in their production, which include physical upgrading, microbiological processes, thermochemical processes , and chemical processes, as described in Figure below:-


Agriculture
Forestry
Biomaterials
residues (straw, grass cuttings), biogas, energy crops
forest residues + SRF: wood chips, pellets
Food Industry
Waste managment
Wood, Pulp & Paper, Furniture Industry
landfill- and sewage treatment gas, biogas from org. wastes, sewage sludge, demolition wood
biogas from sewage treatment, solid bio fuels
saw dust, chips, pellets
Energy Sector
BtL, H2 etc.
SVO, biodiesel, ethanol, biogas (CNG)
Transport Fuels



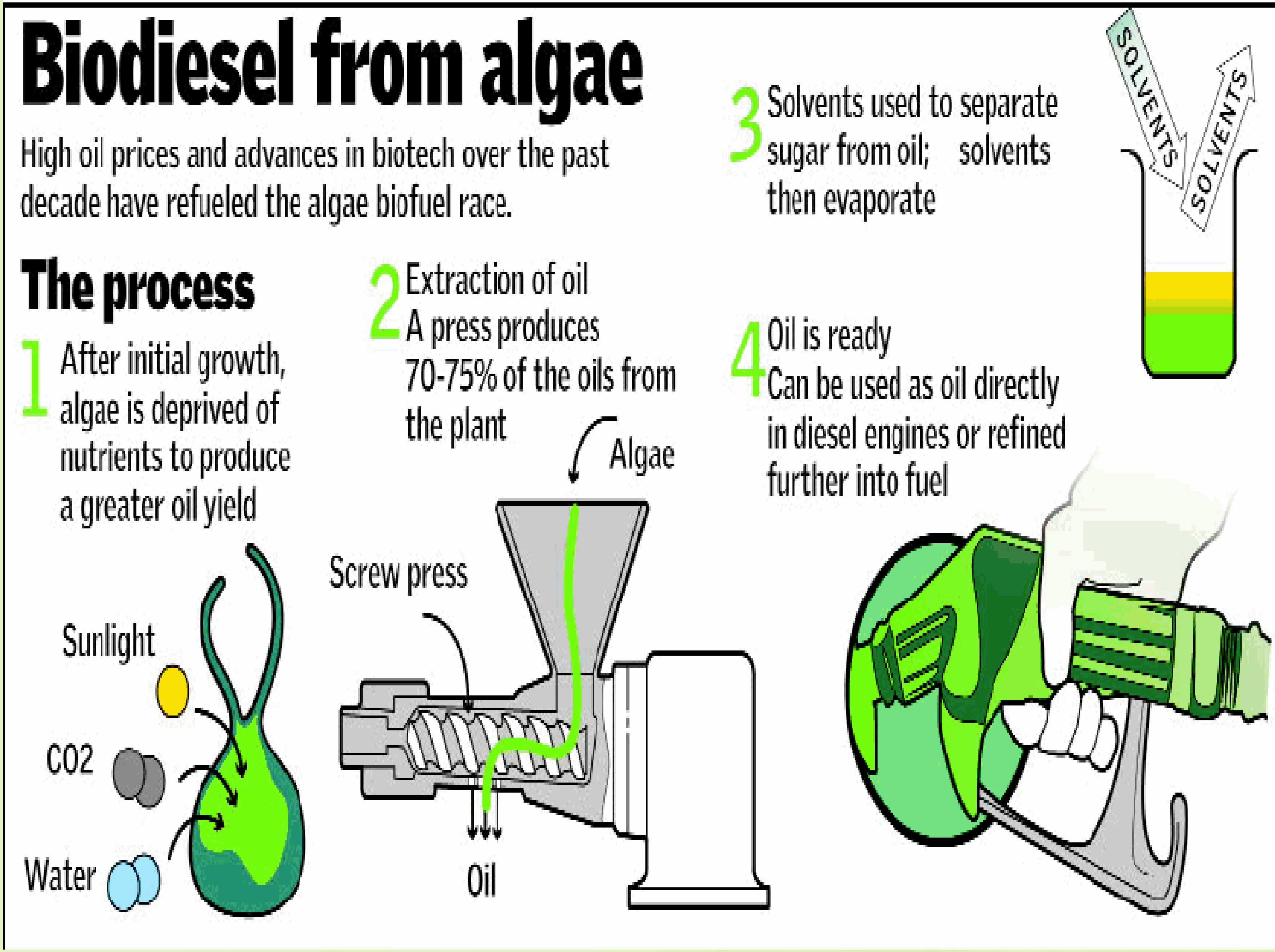
CO_2
CO_2
Electricity
Automobiles
Power plant
Alcohol plant
Tree
plantation
Truck transport
Truck transport

SUGARCANE PRODUCTS: STEP BY STEP

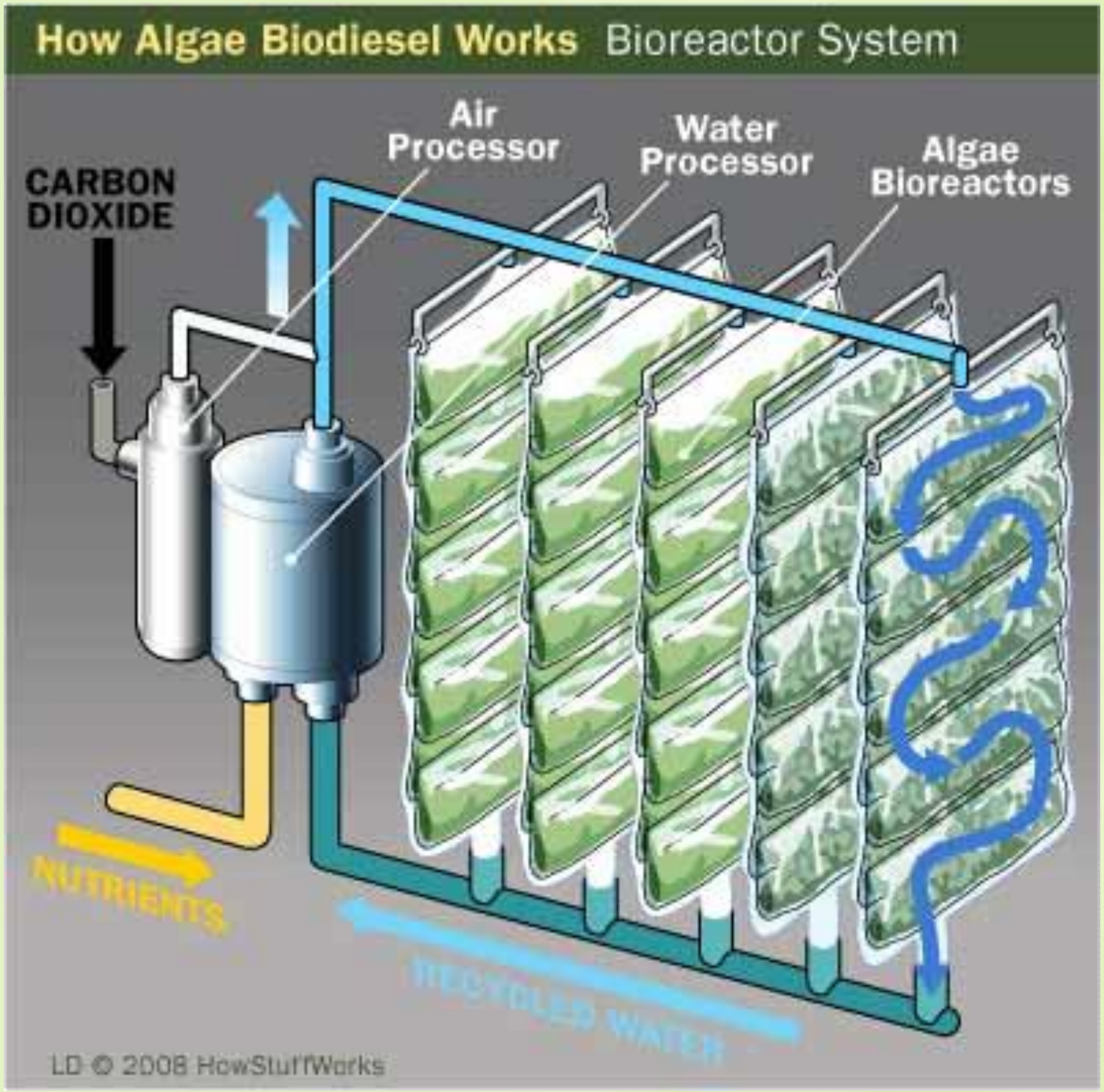


How does algae grow?

- Sunlight, Water & Carbon Dioxide


Biodiesel from algae
High oil prices and advances in biotech over the past decade have refueled the algae biofuel race.
The process
1 After initial growth, algae is deprived of nutrients to produce a greater oil yield
Sunlight
CO2
Water
2 Extraction of oil
A press produces 70-75% of the oils from the plant
Algae
Screw press
Oil
3 Solvents used to separate sugar from oil; solvents then evaporate
SOLVENTS
SOLVENTS
4 Oil is ready
Can be used as oil directly in diesel engines or refined further into fuel

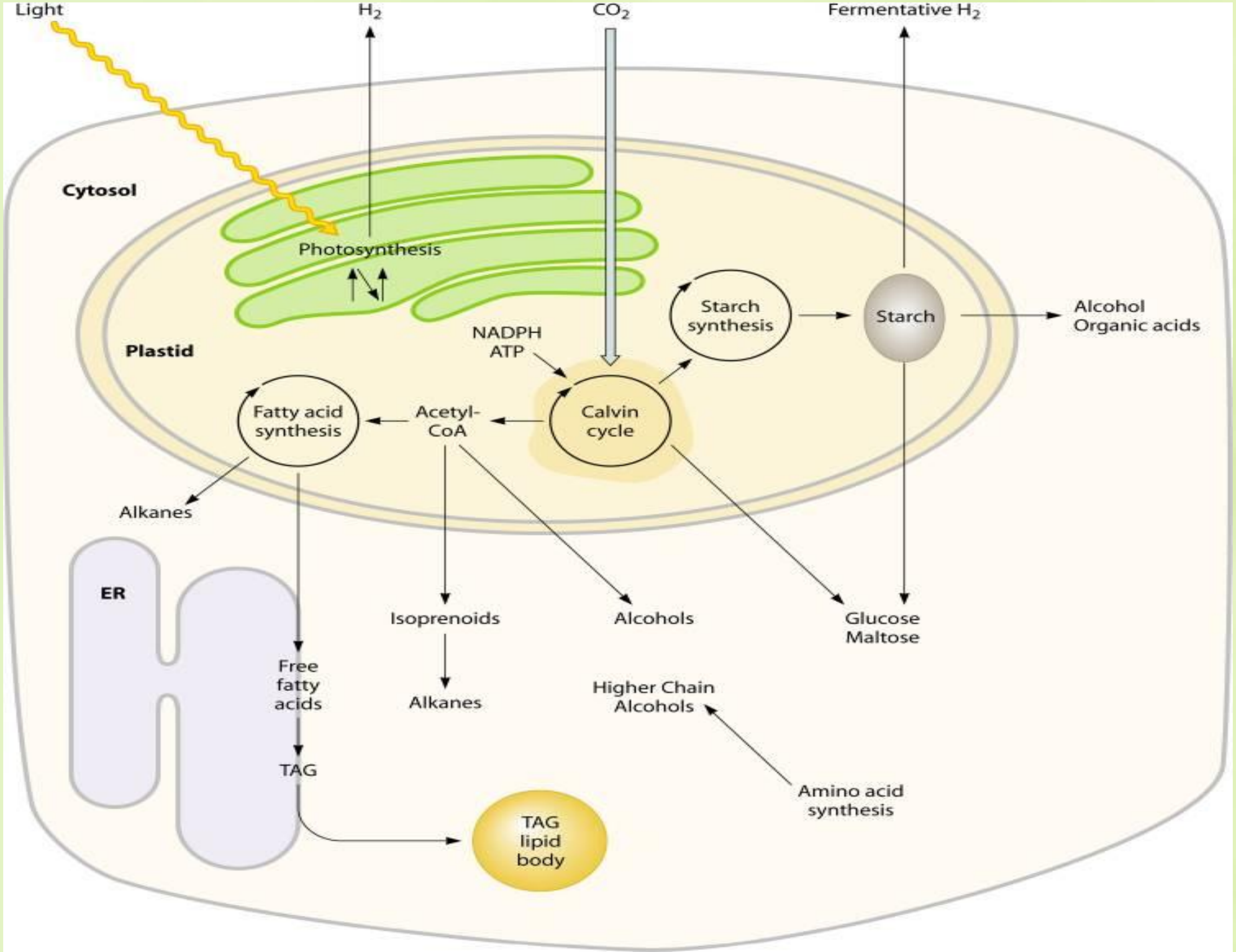
Open Pond Systems

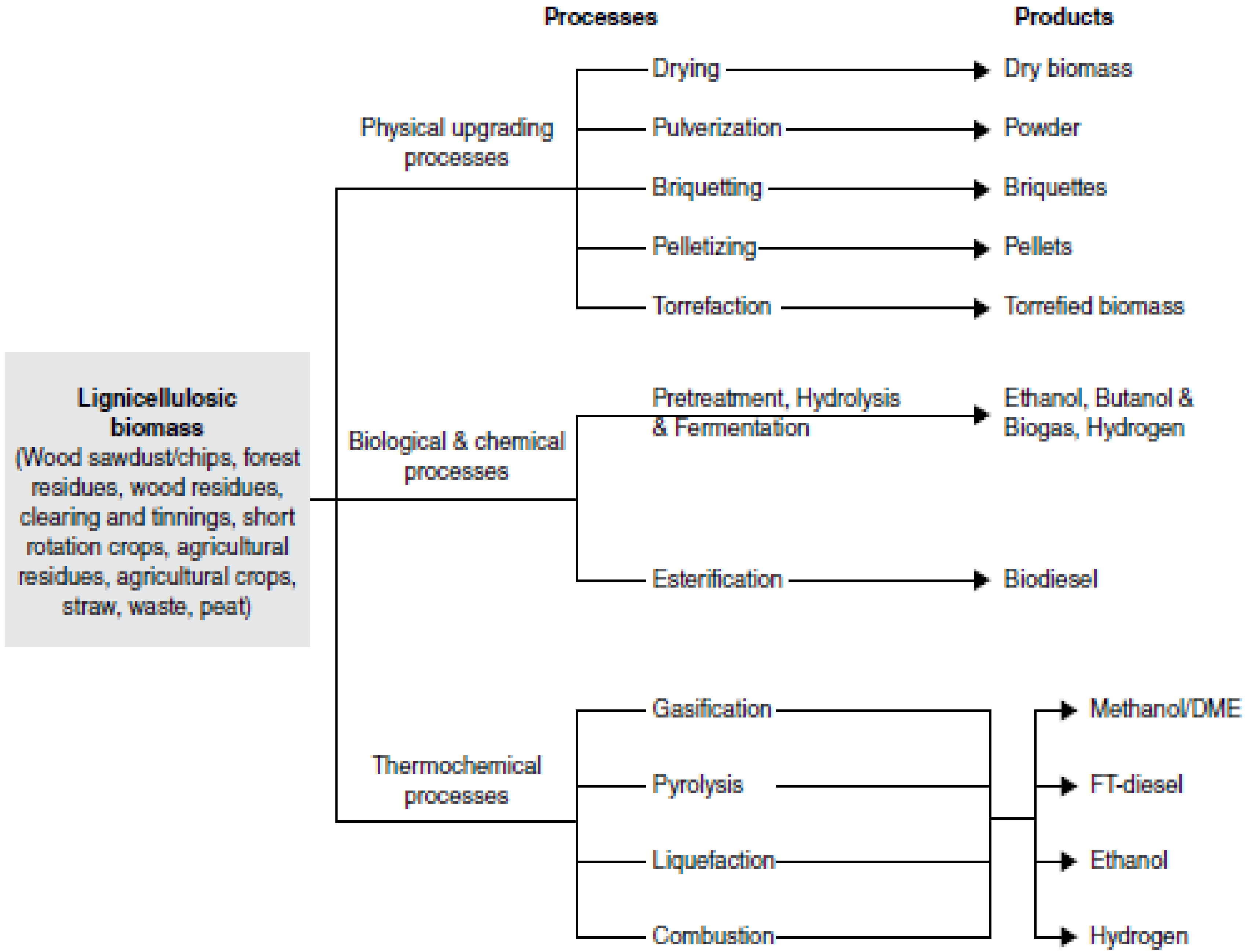

How Algae Biodiesel Works Bioreactor System
Air Processor
Water Processor
Algae Bioreactors
CARBON DIOXIDE
NUTRIENTS
RECYCLED WATER
LD © 2008 HowStuffWorks

Finding the Right Algae

- Over 40,000 species of algae have been identified, likely hundreds of thousands more to be discovered

The Source of Algae Energy





Different types of bioenergy production processes from biomass.

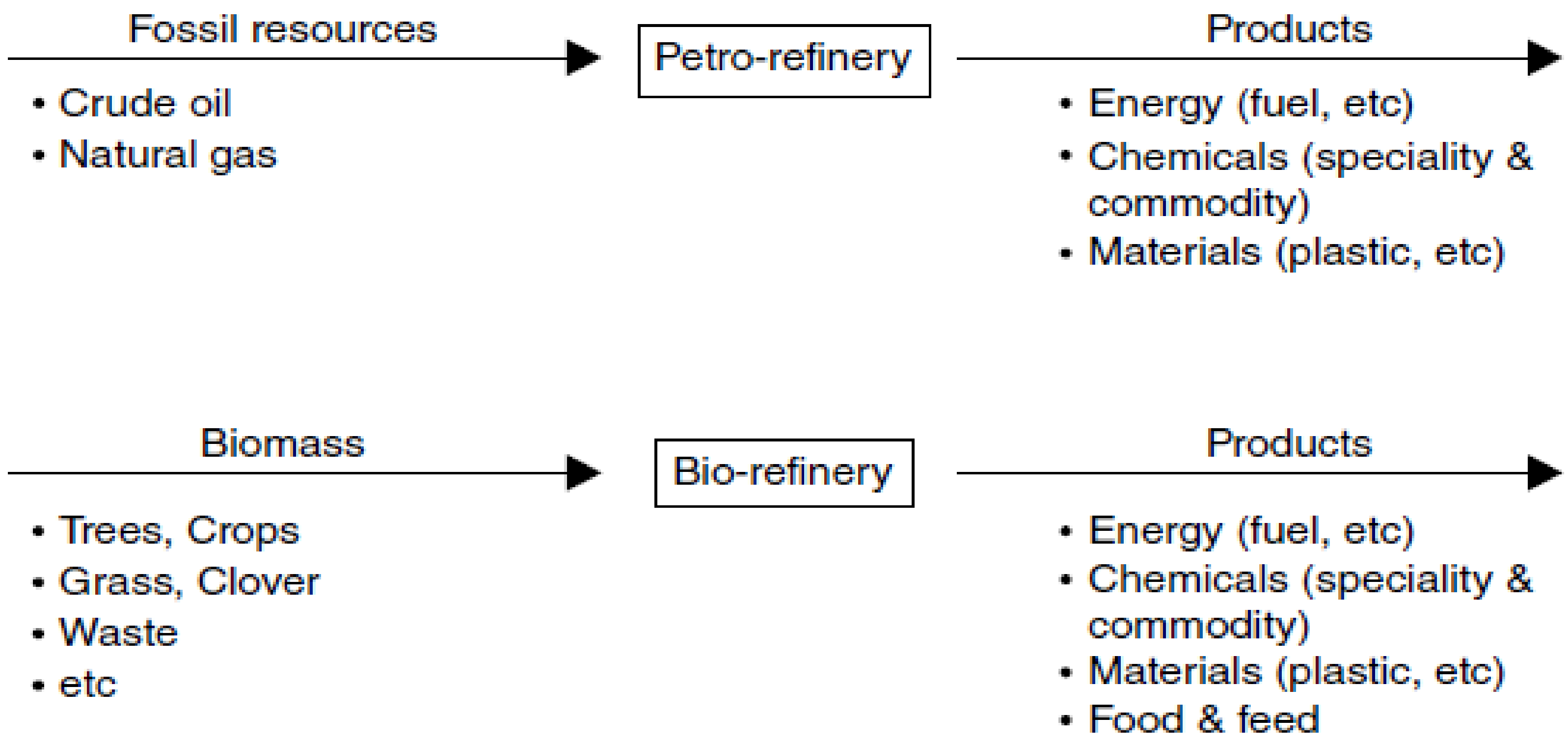
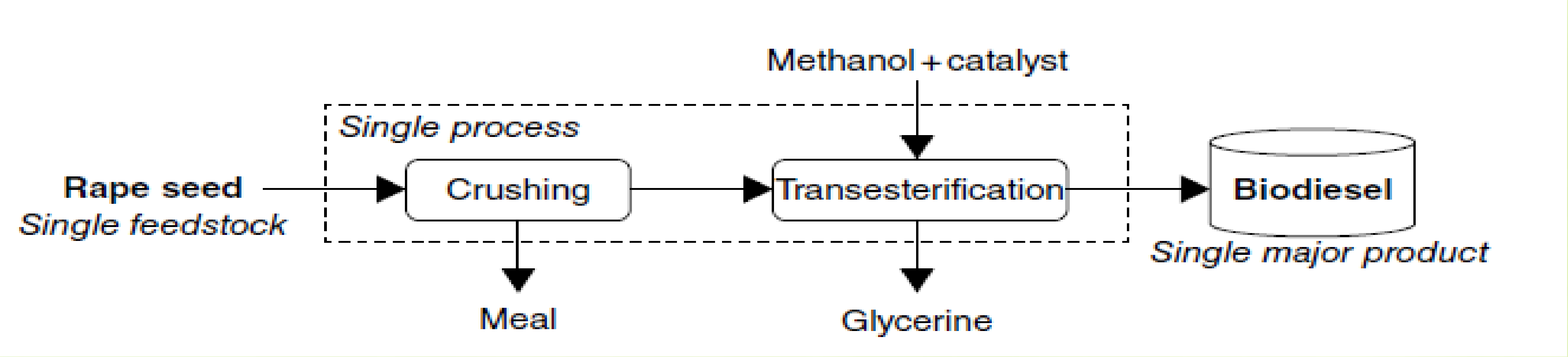


Figure 1.3 *Comparison of petrorefinery v. biorefinery.*

These include low-value high-volume products such as transportation fuels (e.g. biodiesel, bioethanol), commodity chemicals and materials and high-value low-volume products or specialty chemicals such as cosmetics.

• **Phase I biorefinery (single feedstock, single process and single major product);**
• **Phase II biorefinery (single feedstock, multiple processes and multiple major products); and**
• **Phase III biorefinery (multiple feedstocks, multiple processes and multiple major products).**



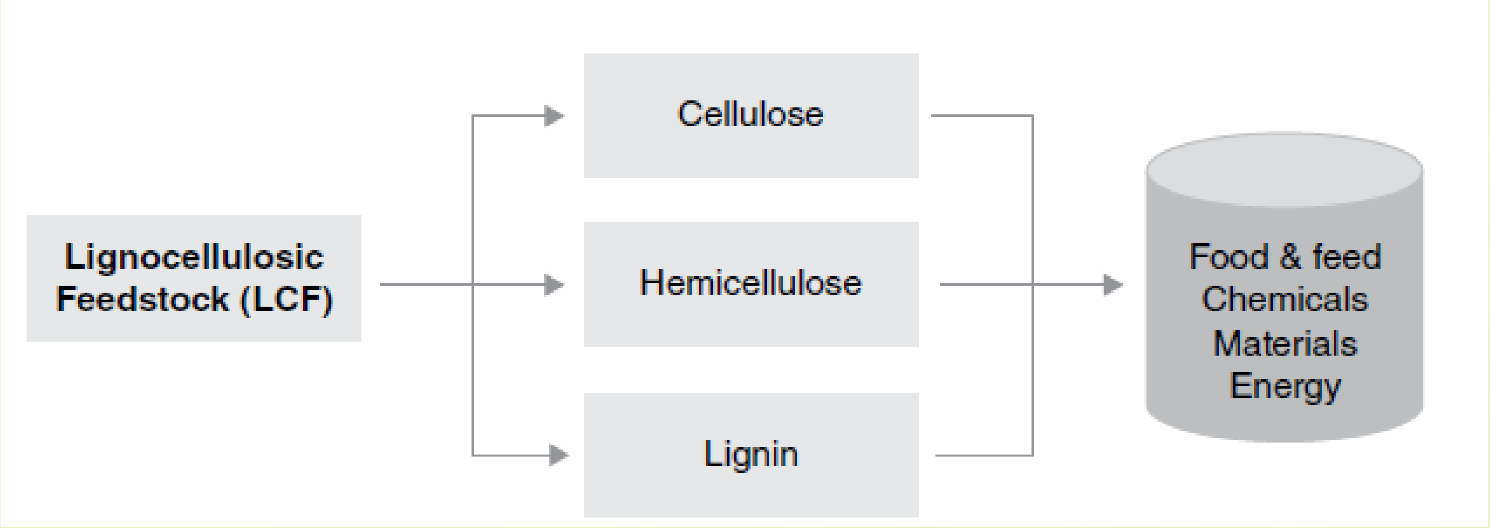


Table 2.1 Various types of long-chain aliphatic compounds found in plant waxes.

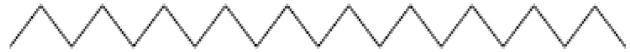
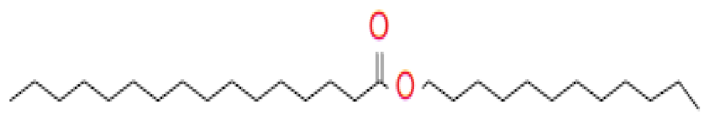
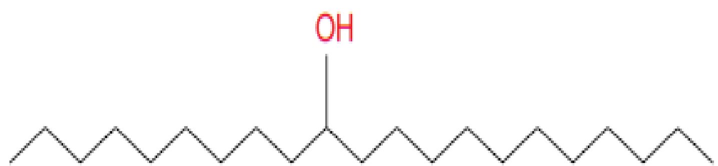
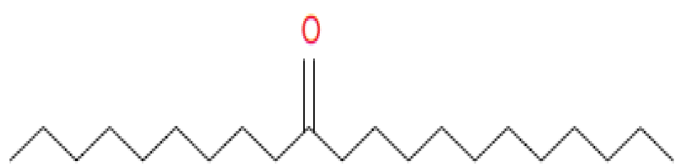
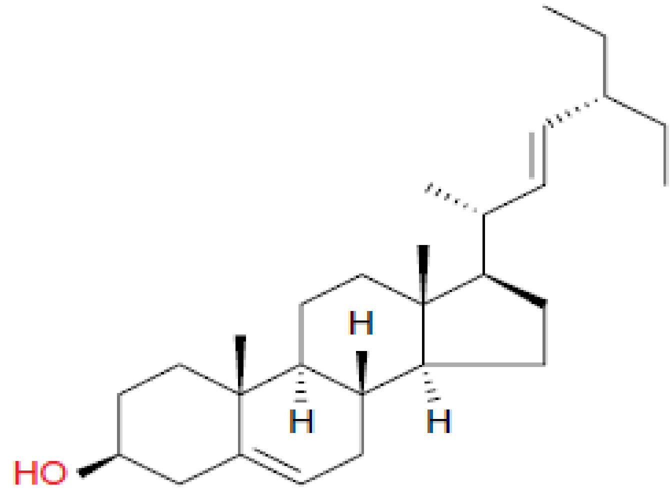
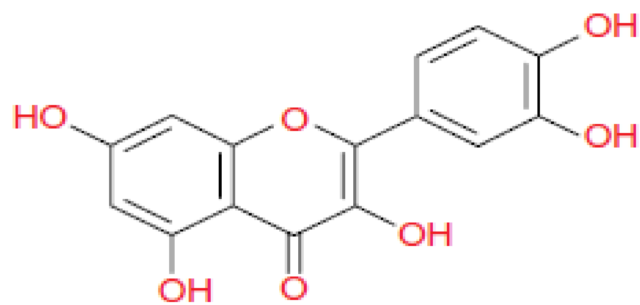
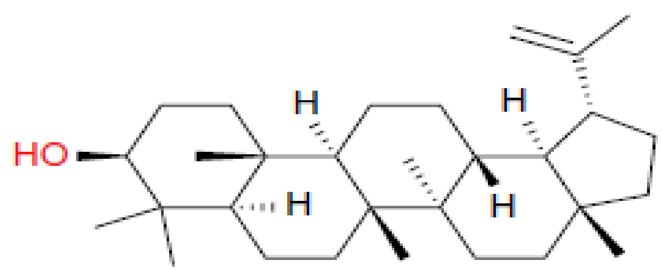
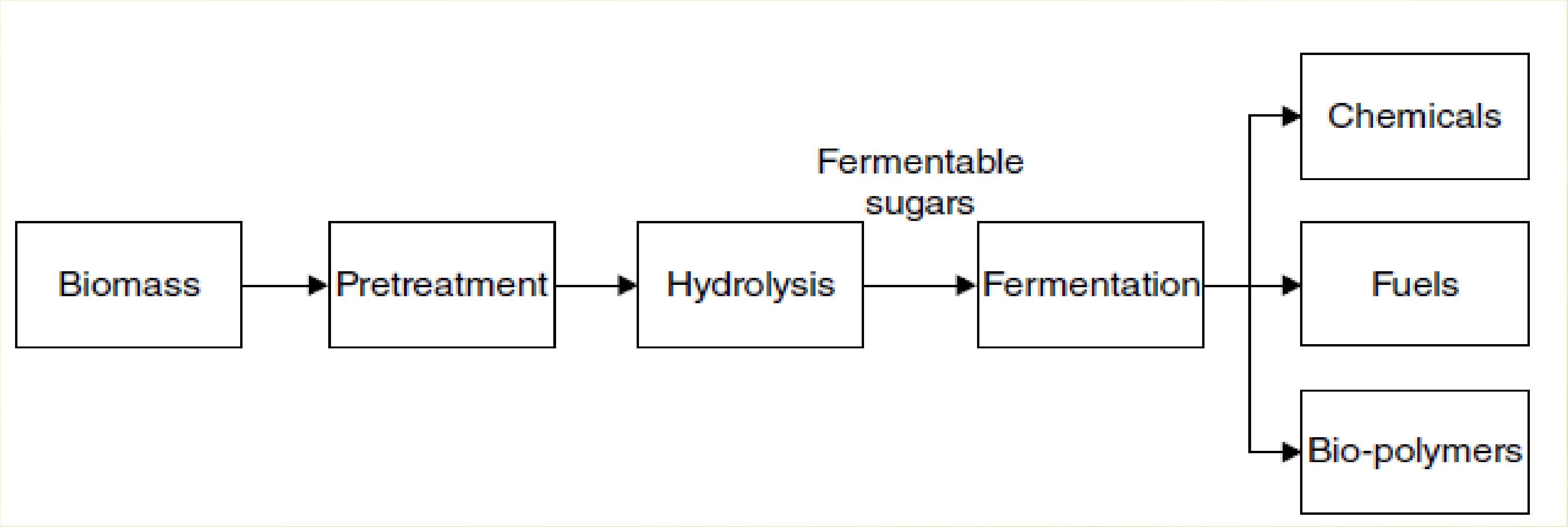
Aliphatic compounds	Structure	Chain length	Preferred no. C atoms
n-alkanes		C_{19}–C_{37}	Odd
Primary alcohols		C_{12}–C_{36}	Even
Aldehydes		C_{14}–C_{34}	Even
Fatty acids		C_{12}–C_{36}	Even
Wax esters		C_{30}–C_{60}	Even
Secondary alcohols		C_{21}–C_{33}	Odd
Ketones		C_{25}–C_{33}	Odd
β-Diketones		C_{27}–C_{35}	Odd

Table 2.2 Major cyclic compounds found in plant waxes.

Cyclic compounds	Structure
Sterols	
Flavonoids	
Terpenoids	

Biological Processing
Fermentation

Fermentation involves the use of microorganisms such as bacteria and fungi to transform sugars into products. Bioconversion of biomass into products through fermentation is a very flexible process which could lead to a wide range of products including biofuels, biochemicals, or biomaterials



Anaerobic Digestion

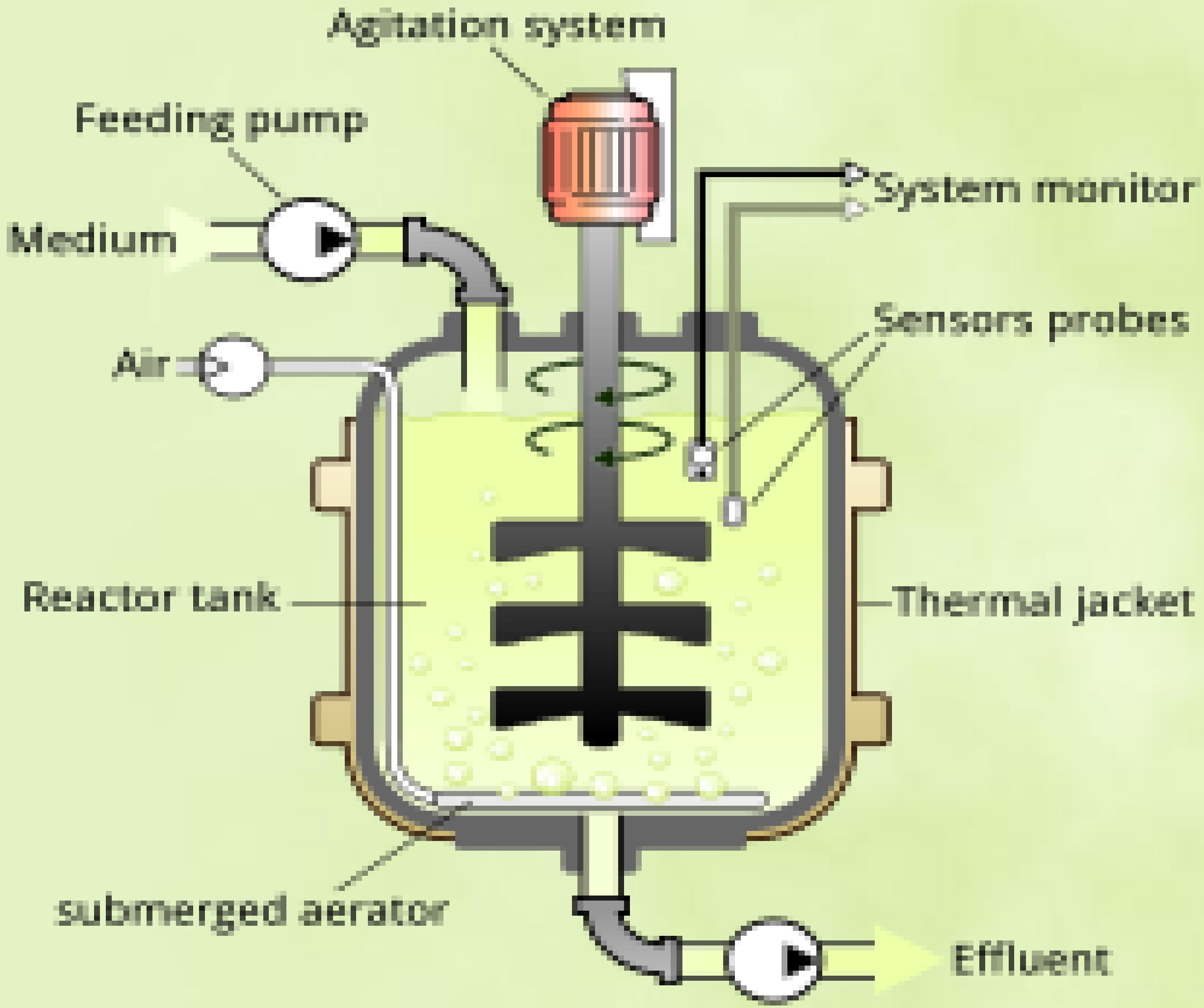
Anaerobic digestion (AD) involves a mixture of bacteria including syntrophic bacteria, fermentative bacteria, acetogenic bacteria and methanogenic bacteria to decompose biomass under anaerobic conditions in order to produce biogas (methane and hydrogen) as fuel.

The process is divided into four stages:

hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In the hydrolysis stage, insoluble organic compounds are broken down into water-soluble monomers by hydrolases secreted by a consortium of bacteria.

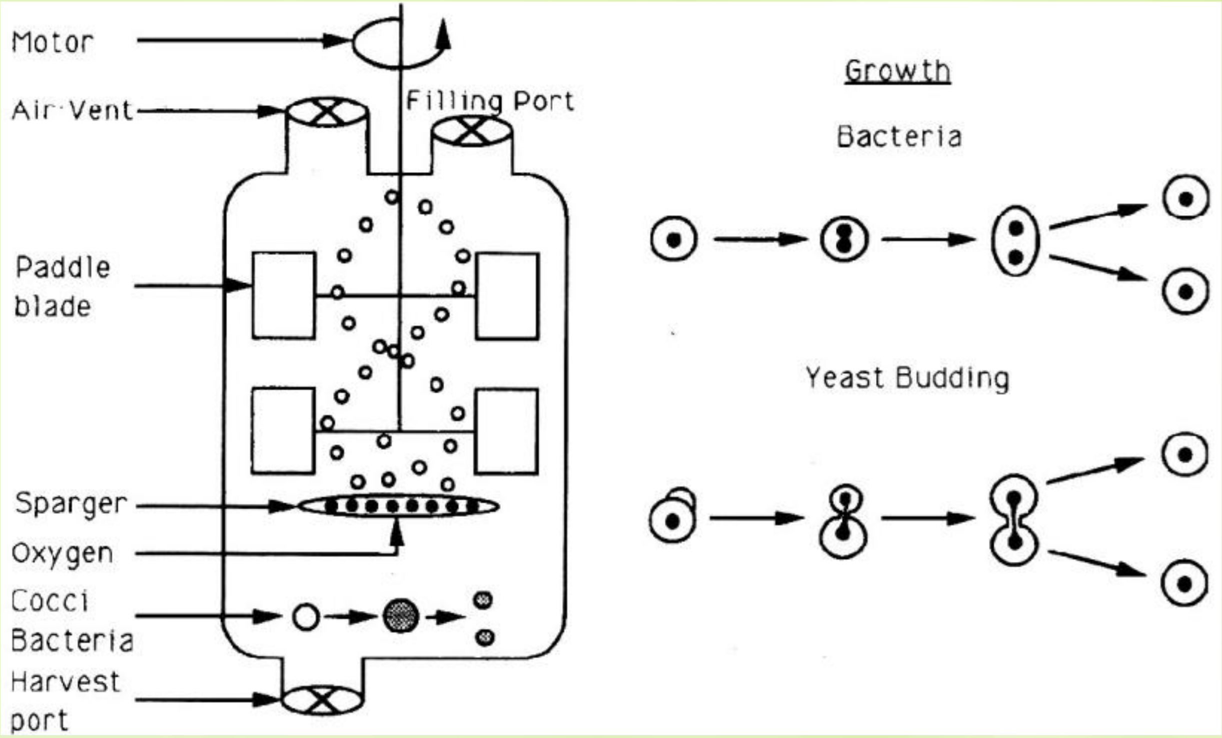
The barely decomposable polymer, which is not decomposed by hydrolases, remains solid and thus limits the efficiency of AD. The products of hydrolysis are then converted into short-chain organic acids, alcohols, aldehydes, and carbon dioxide in the acidogenesis stage and transformed into acetates, carbon dioxide, and hydrogen in the acetogenesis stage. Finally, methanogenic bacteria utilize acetic acid, hydrogen, and carbon dioxide to produce methane. About 70% of the methane is converted from acetic acid while the remaining 30% results from carbon dioxide reduction. Biogas and digestate, which is the remaining solids with the mineralized nutrient, are the final products .

(Bioreactor)


Agitation system
Feeding pump
Medium
System monitor
Air
Sensors probes
Reactor tank
Thermal jacket
submerged aerator
Effluent

Bacteria, fungal, and yeast or some cells plant or animals used in bioreactor

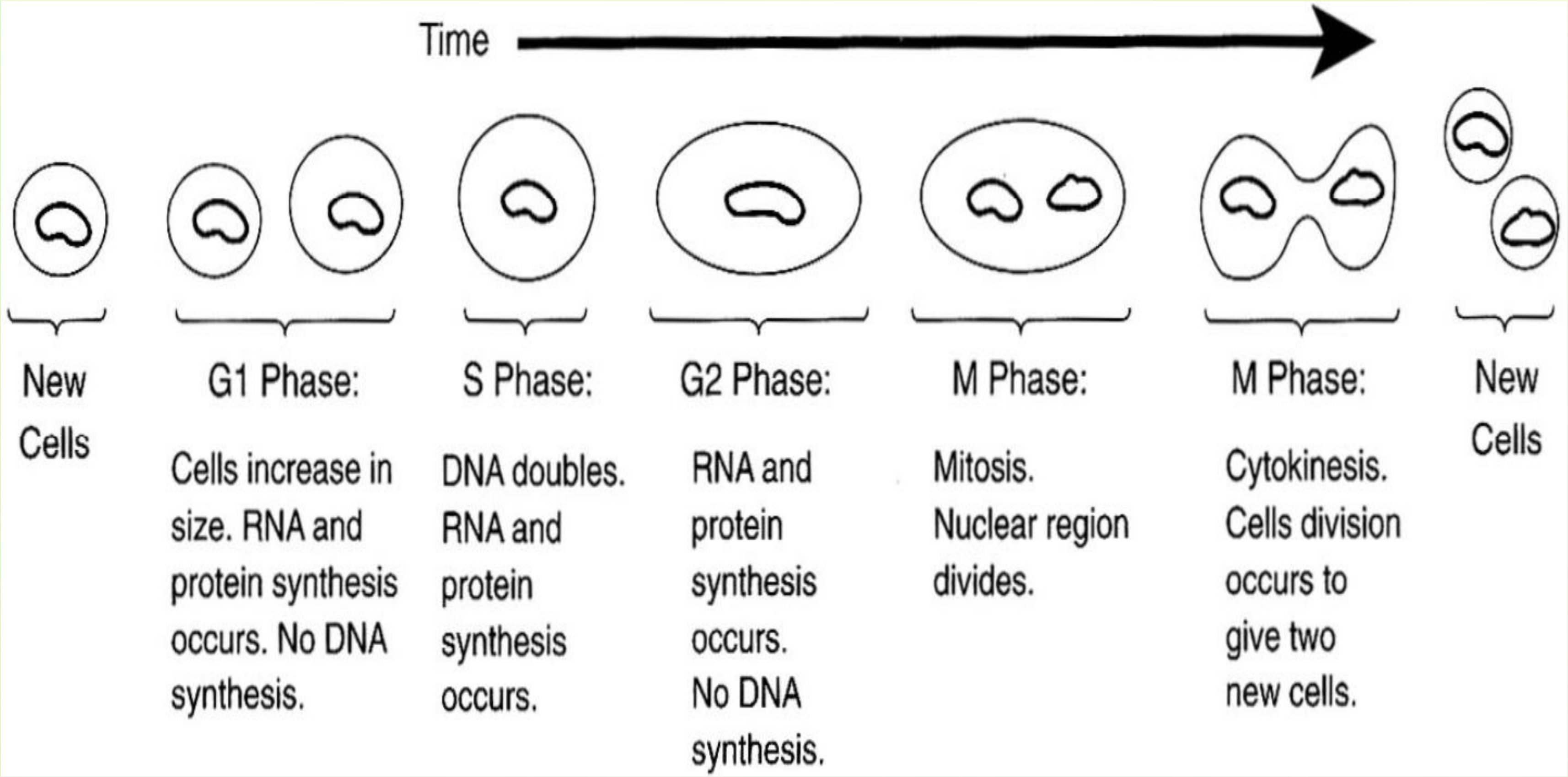
Batch Bioreactor

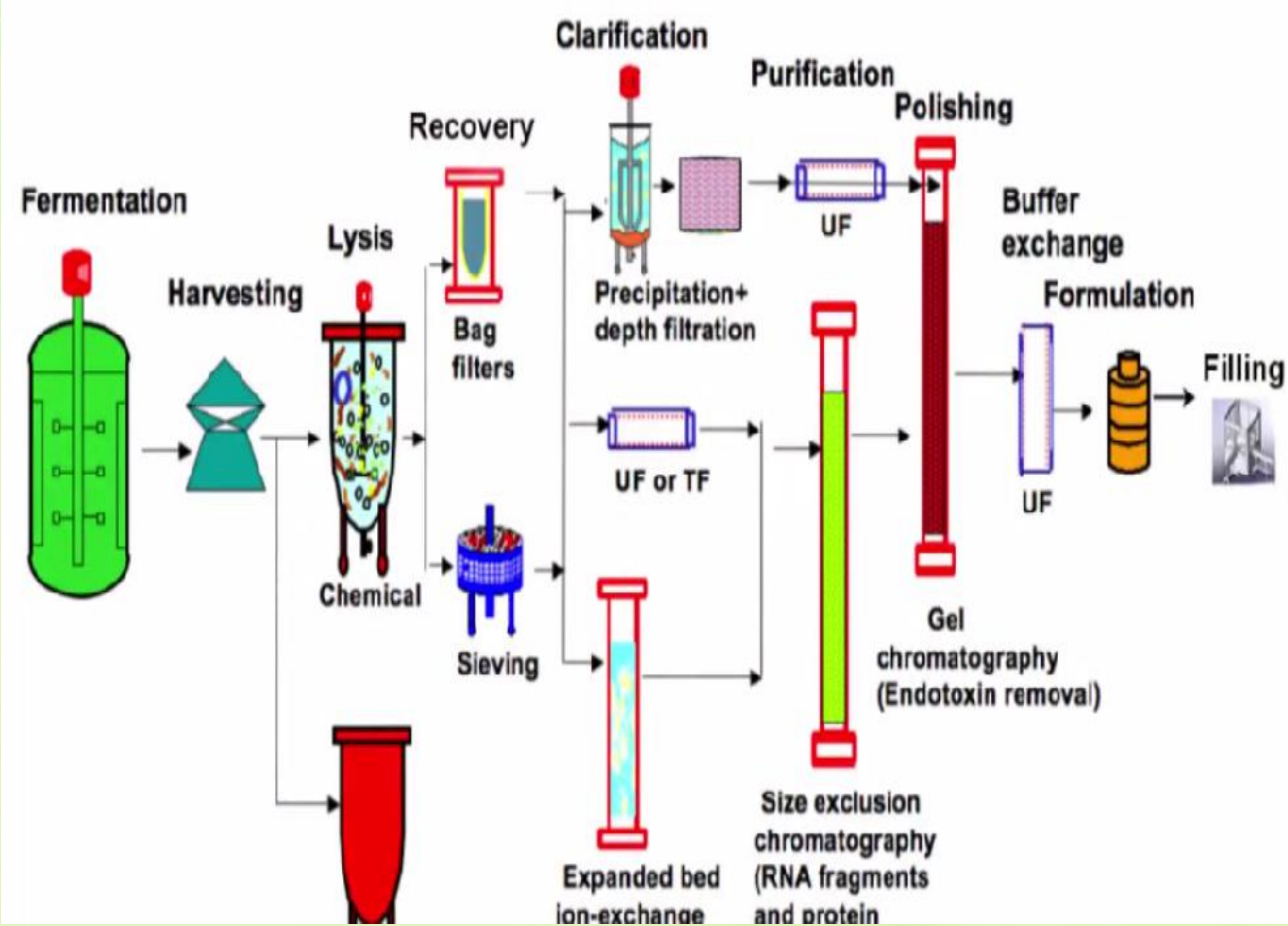


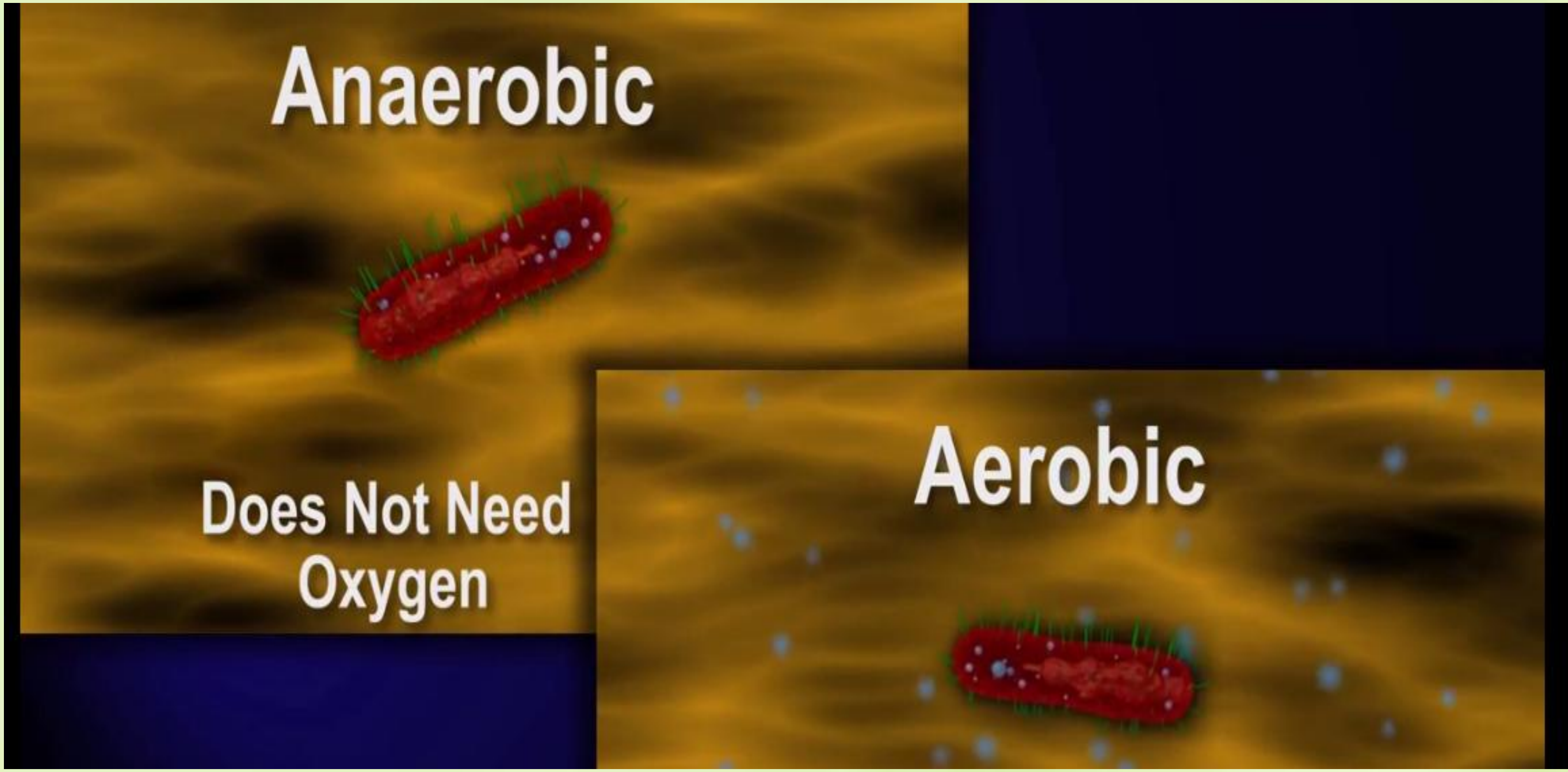
$$[\text{Cells}] + \begin{bmatrix}\text{Carbon}\\ \text{source}\end{bmatrix} + \begin{bmatrix}\text{Nitrogen}\\ \text{source}\end{bmatrix} + \begin{bmatrix}\text{Oxygen}\\ \text{source}\end{bmatrix} + \begin{bmatrix}\text{Phosphate}\\ \text{source}\end{bmatrix} + \cdots$$

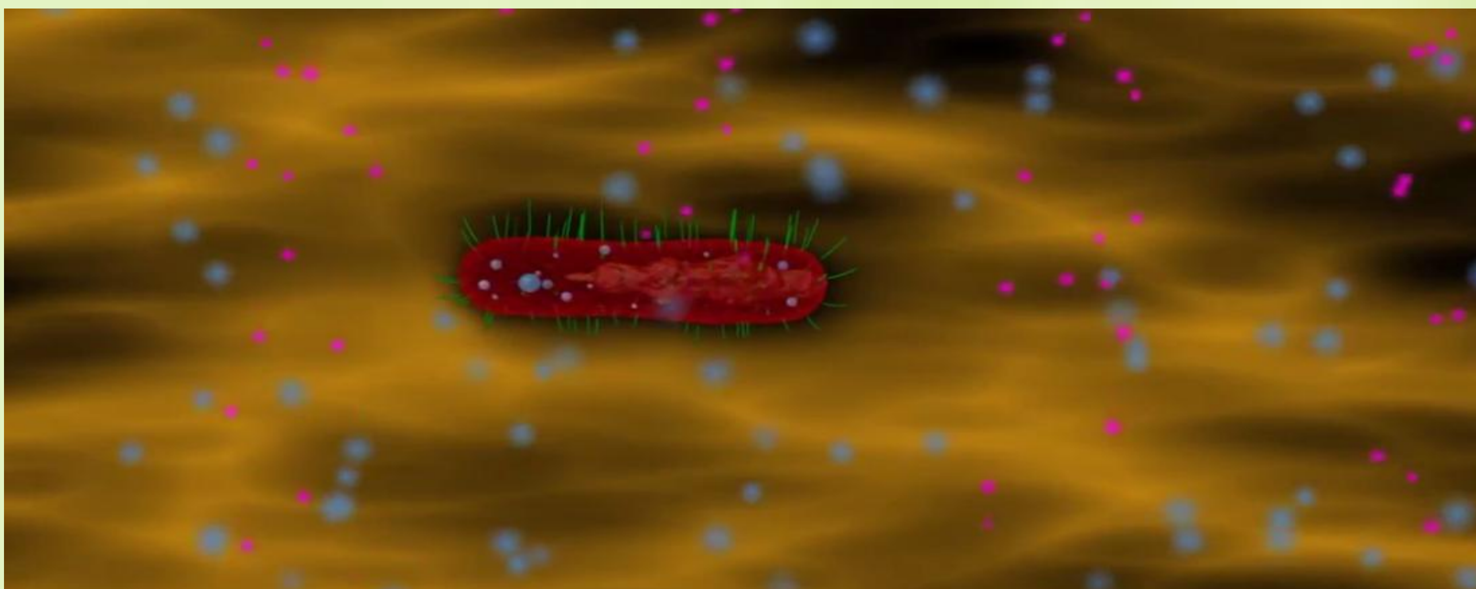
$$\xrightarrow{\text{Culture media conditions (pH, temperature, etc.)}} [CO_2] + [H_2O] + [\text{Products}] + \begin{bmatrix}\text{More}\\ \text{cells}\end{bmatrix}$$

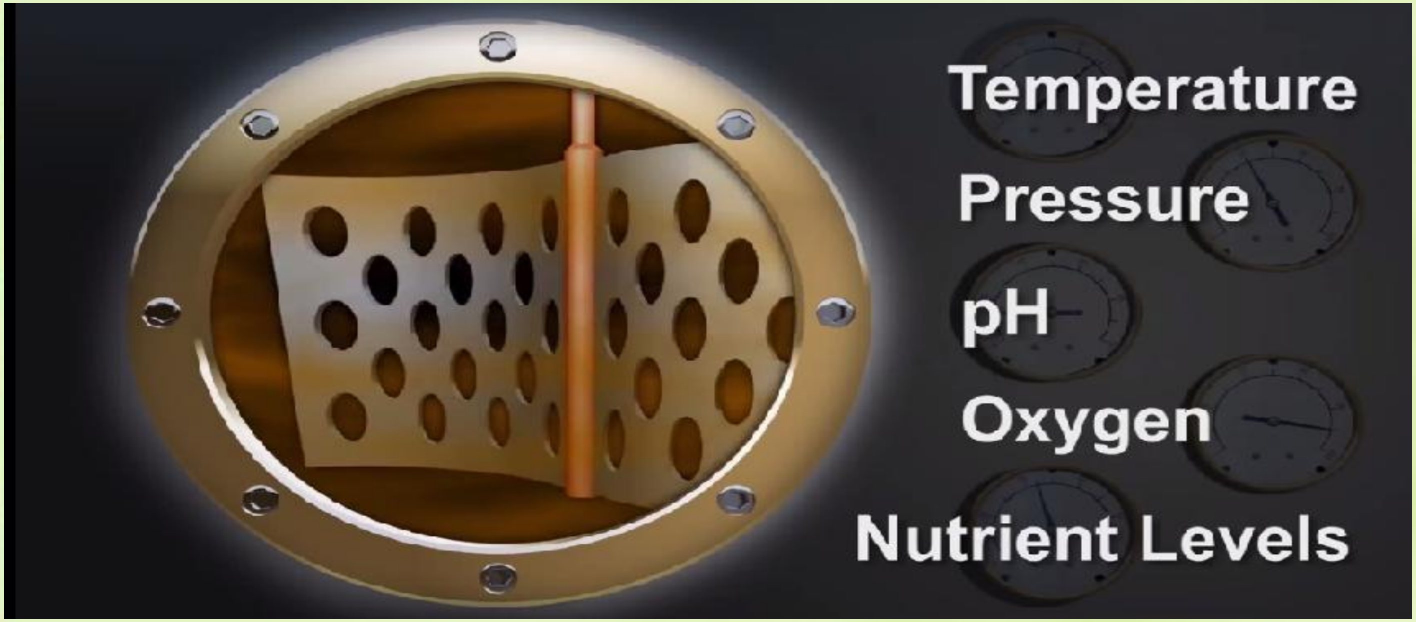
Phases of Cell Growth and Division

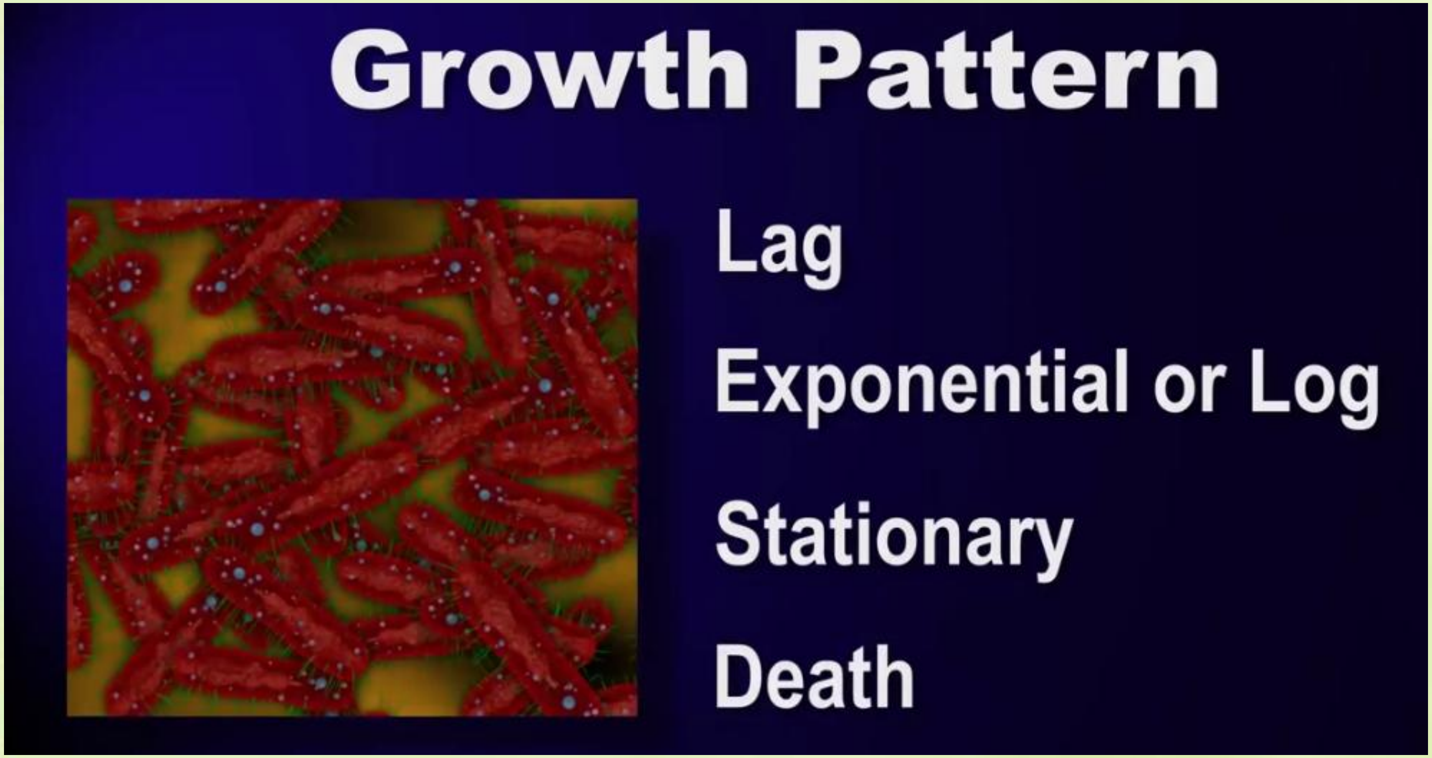


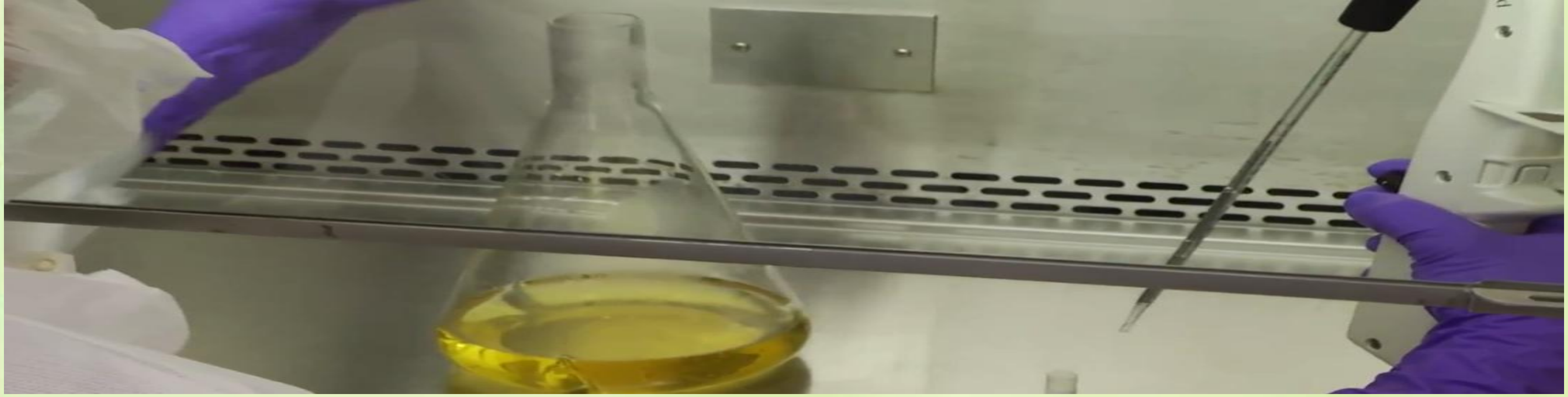

Clarification
Purification
Polishing
Recovery
Fermentation
Lysis
Harvesting
Buffer exchange
UF
Precipitation+ depth filtration
Formulation
Bag filters
Filling
UF or TF
UF
Chemical
Sieving
Gel chromatography (Endotoxin removal)
Size exclusion chromatography (RNA fragments and protein
Expanded bed ion-exchange

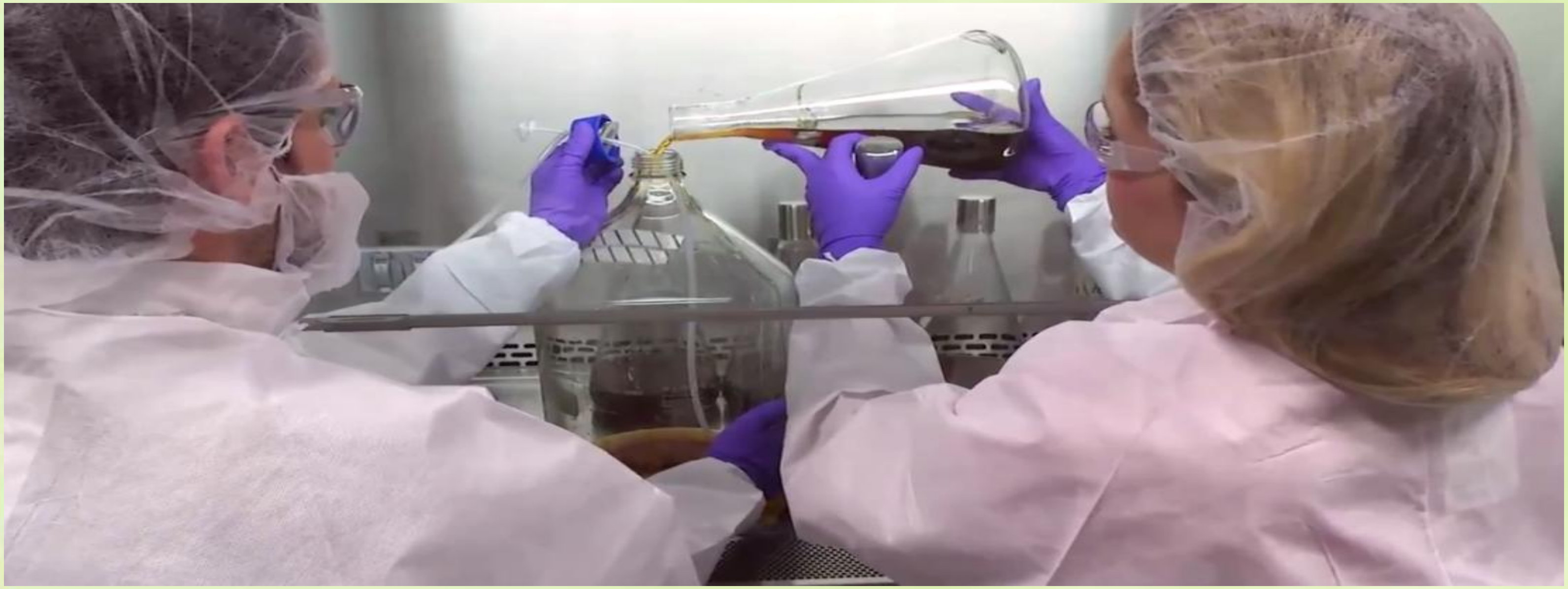

Anaerobic
Does Not Need Oxygen
Aerobic




Temperature
Pressure
pH
Oxygen
Nutrient Levels

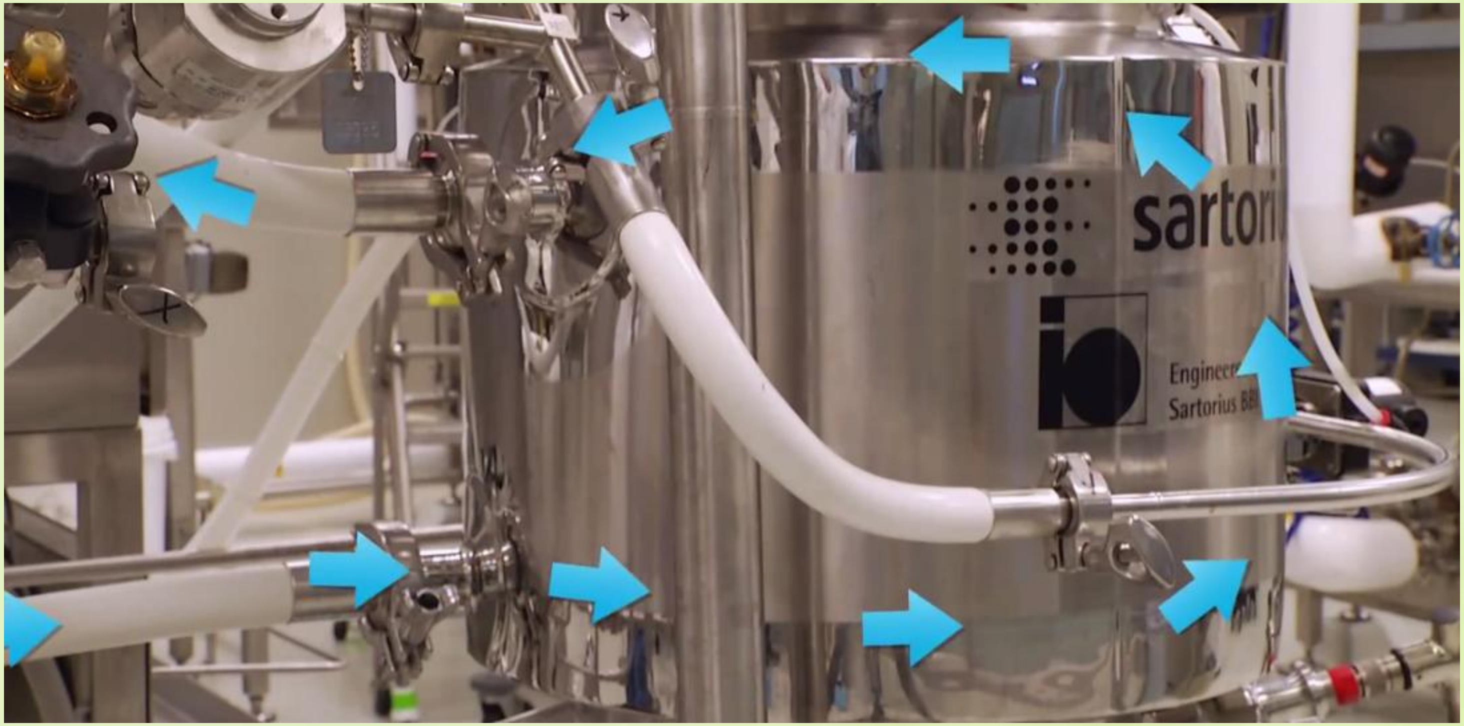

Growth Pattern
Lag
Exponential or Log
Stationary
Death





Basic Ingredients

- Nutrients
- Stabilizers
- Antibiotic
- Anti-Foaming Agent
- IPTG (Biochemical Inducer)



Preparation

Removing Equipment and Materials

Cleaning and Sanitizing

Sterilizing Equipment as required by the SOP

Ingredients

Yeast Extract

Tryptic Soy Broth

Ammonium Chloride

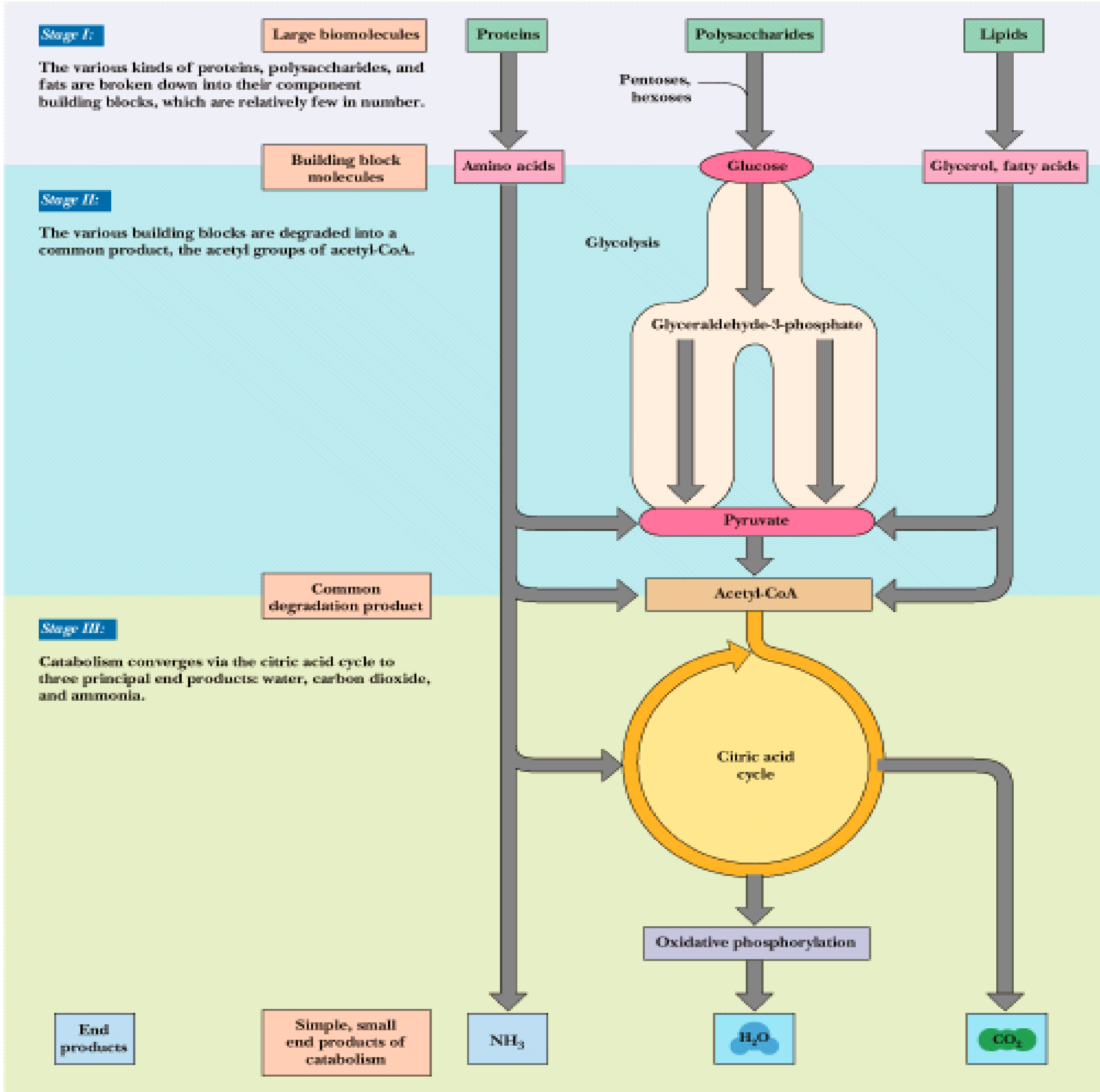
Sodium Biphosphate

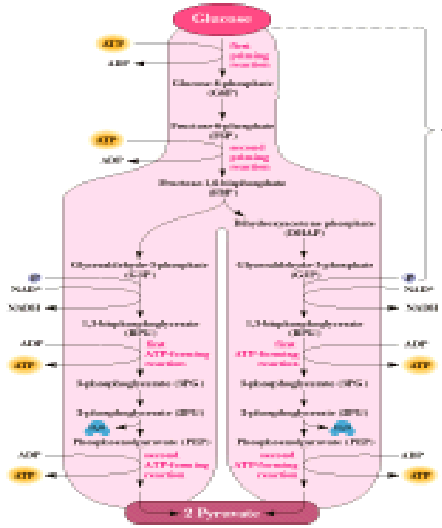
Monopotassium Phosphate

Antifoam Compound

Monitoring

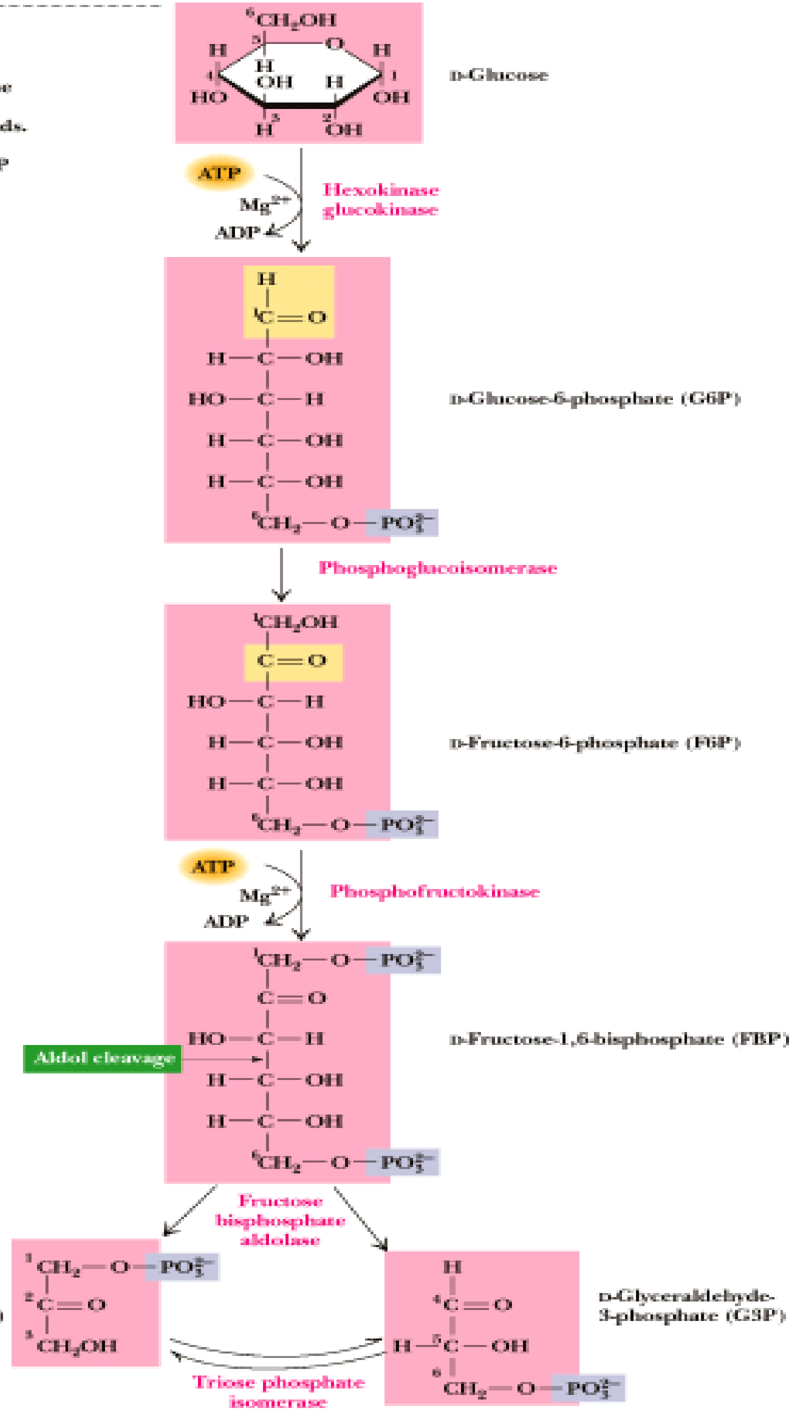
- Batch Temperature
- Agitator RPMs
- Dissolved Oxygen Levels
- pH
- Vessel Pressure
- Optical Density
- Air Flow Rate
- Glucose Concentrations

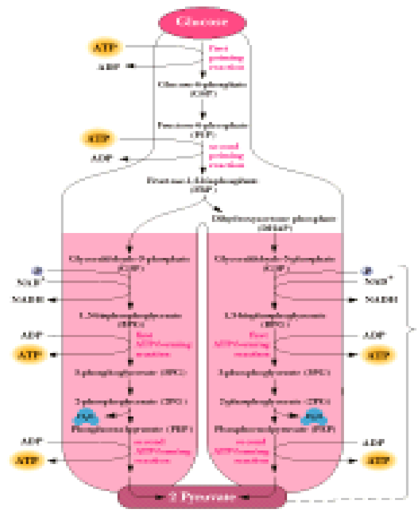

Stage I:
Large biomolecules
Proteins
Polysaccharides
Lipids
The various kinds of proteins, polysaccharides, and fats are broken down into their component building blocks, which are relatively few in number.
Pentoses, hexoses
Building block molecules
Amino acids
Glucose
Glycerol, fatty acids
Stage II:
The various building blocks are degraded into a common product, the acetyl groups of acetyl-CoA.
Glycolysis
Glyceraldehyde-3-phosphate
Pyruvate
Common degradation product
Acetyl-CoA
Stage III:
Catabolism converges via the citric acid cycle to three principal end products: water, carbon dioxide, and ammonia.
Citric acid cycle
Oxidative phosphorylation
End products
Simple, small end products of catabolism
NH_3
H_2O
CO_2



In the first five steps of glycolysis, one six-carbon molecule of glucose is split into two 3-carbon compounds.

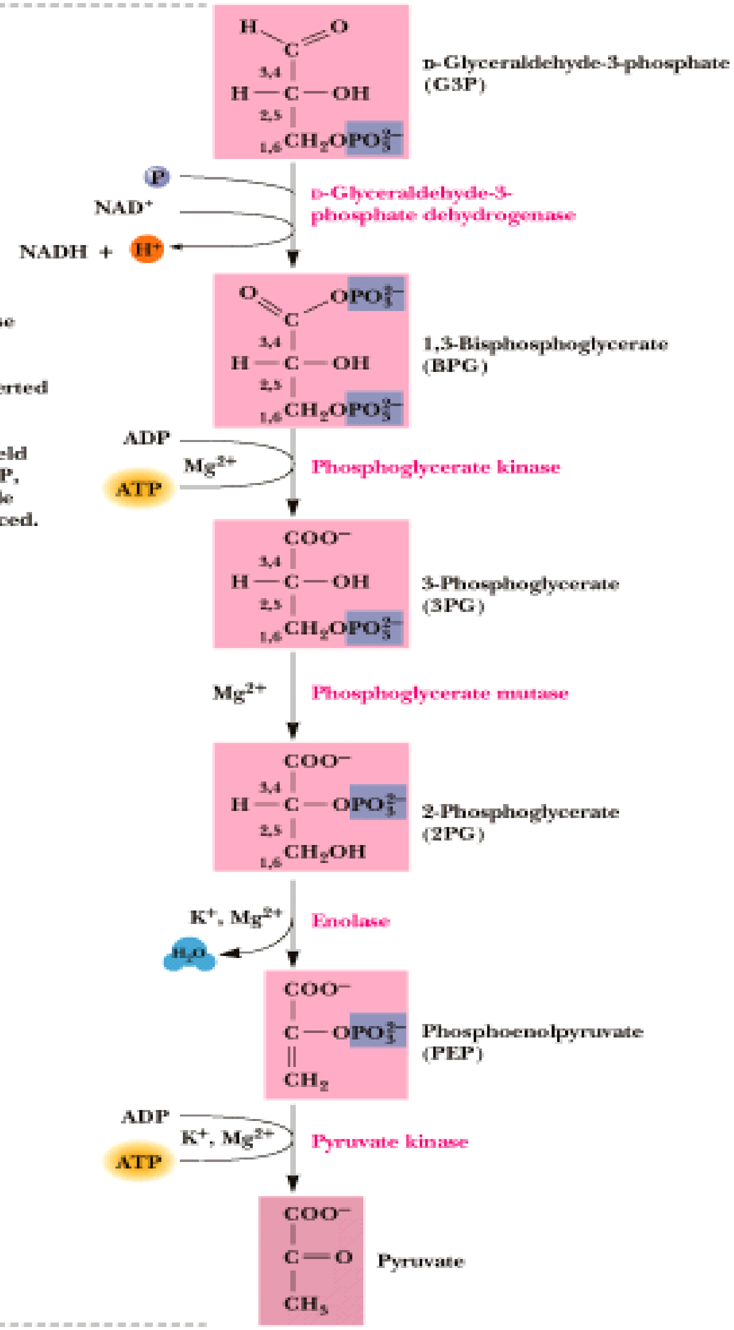
2 molecules of ATP are required to prime these reactions.





In the second phase of glycolysis, glyceraldehyde-3-phosphate is converted to pyruvate.

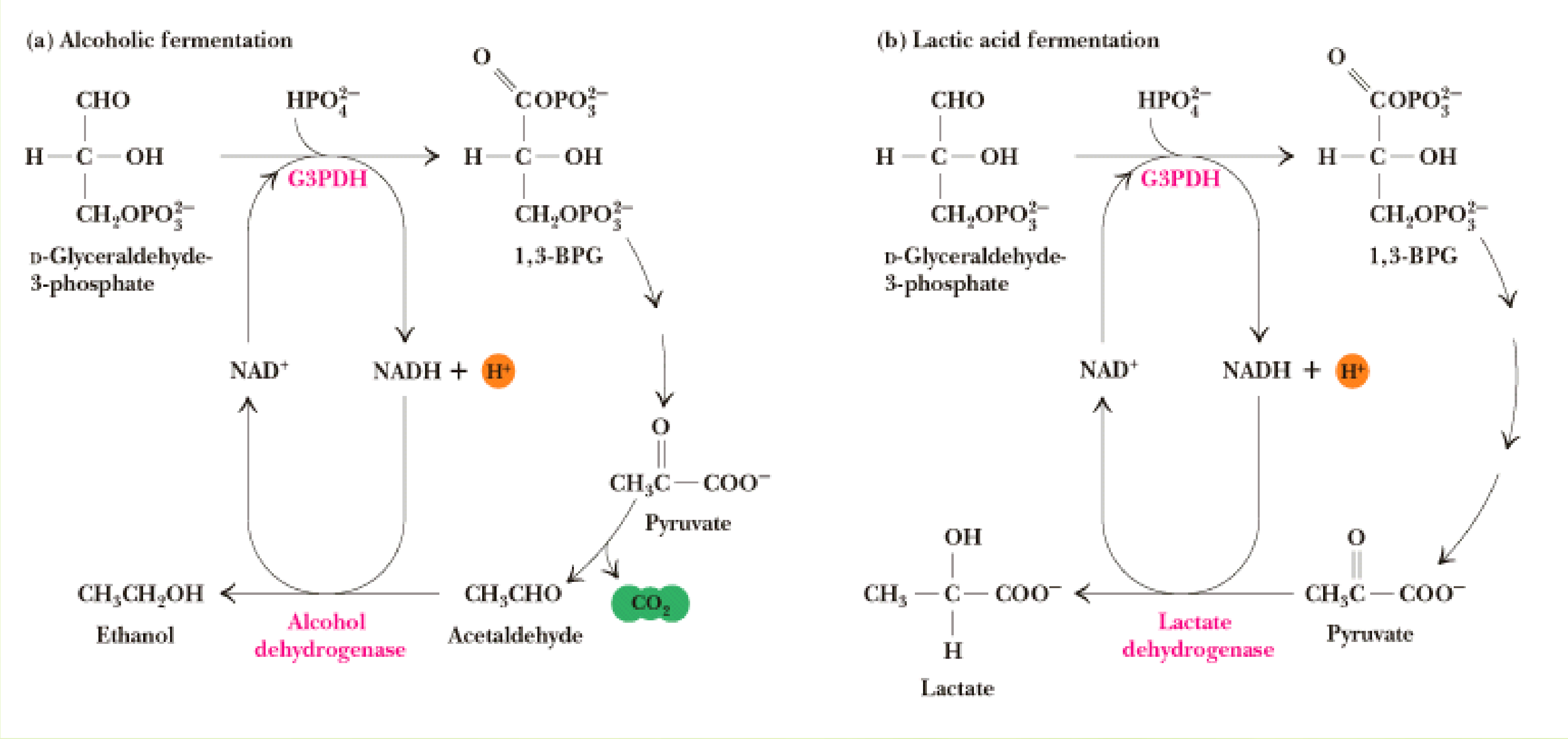
These reactions yield 4 molecules of ATP, 2 for each molecule of pyruvate produced.



The Fate of NADH and Pyruvate Aerobic or anaerobic??

Pyruvate is also energy - two possible fates:

- aerobic: citric acid cycle
- anaerobic: LDH makes lactate



Microbiological Processes For Hydrogen Production:-

Various microbial processes can be exploited to utilize energy that has been stored in biomass by photosynthesis. These processes can generate useful biofuels such as hydrogen, butanol, and biogas. Moreover, biomass can be converted into ethanol; this is commonly done using fungi but can also be achieved with bacteria. Finally, certain algae can be used to produce biodiesel

The hydrogenase reaction has the following stoichiometric formula:

$$2H^{+} \leftrightarrow H_2 + 2e^{-}$$

As indicated above, the process is reversible so hydrogen may either be produced or consumed. Four categories of hydrogen-related processes and organisms that perform them have been delineated as listed below:

1. photoautotrophic hydrogen production;
2. photoheterotrophic hydrogen production;
3. heterotrophic hydrogen production; and
4. heterotrophic hydrogen production coupled to photo-production.

There are three microbial groups that have been studied for biological hydrogen production as shown in Table.1. The first group consists of the cyanobacteria that are autotrophs and directly decompose water to hydrogen and oxygen in the presence of light energy by photosynthesis. Since this reaction requires only water and sunlight and generates oxygen, it is attractive from an environmental perspective. However, the cyanobacteria examined thus far show rather low rates of hydrogen production and may have difficulty overcoming large Gibb’s free energy (+237 kJ/mol hydrogen) requirements.

The second and third groups of bacteria are heterotrophs and use organic substrates as a carbon source for hydrogen production. The heterotrophic microorganisms produce hydrogen under anaerobic conditions, both in the presence or absence of light energy. Accordingly, the process is classified as either photofermentation or dark fermentation. Phototrophic purple nonsulfur bacteria produce hydrogen through photofermentation, and nonphototrophic fermentative bacteria produce hydrogen through dark fermentation.

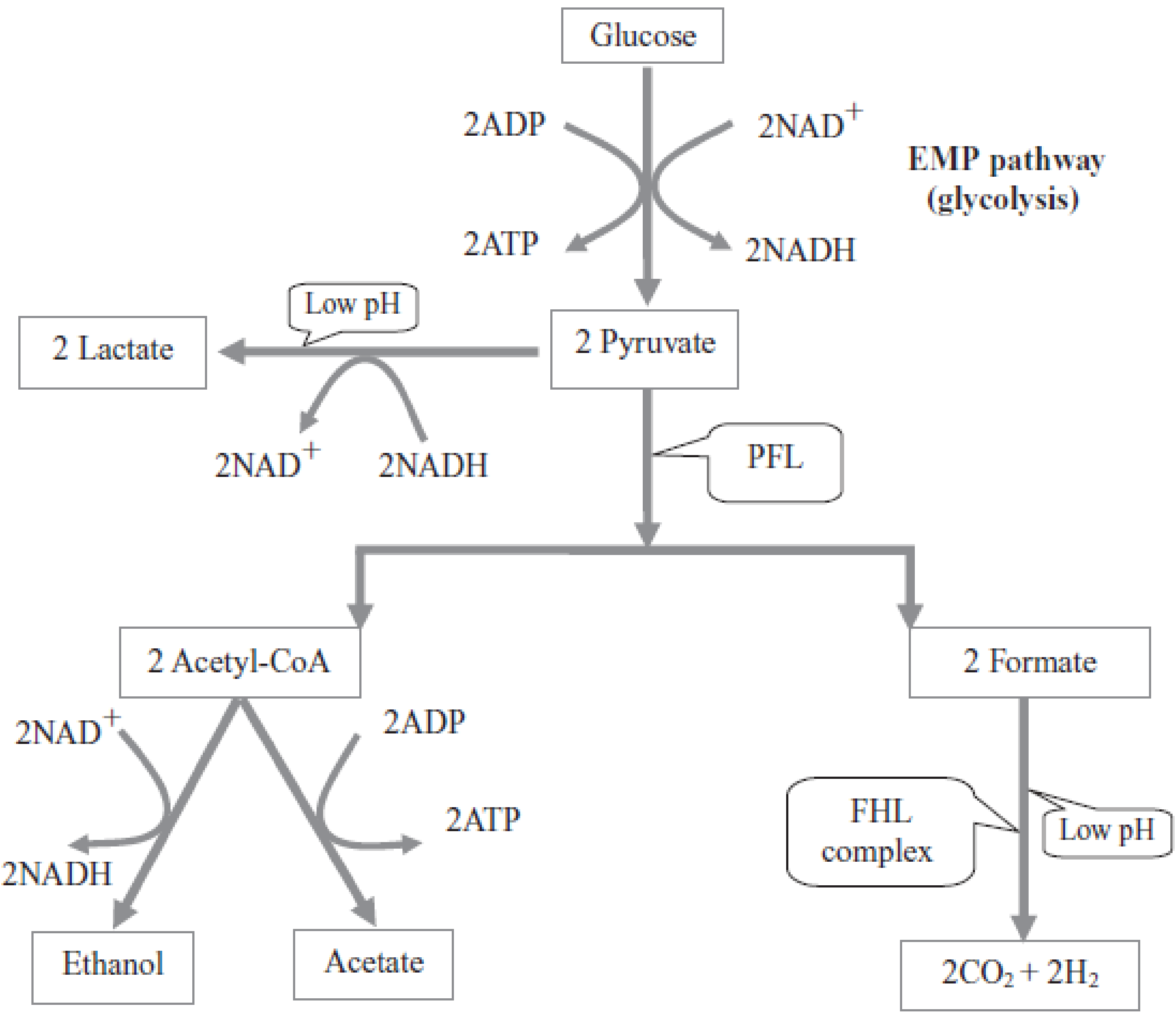
Table 1. Different biological hydrogen production processes.

Biological Process	Microbial Group	Process Description	Disadvantages
Photosynthesis	Cyanobacteria	Cyanobacteria (or blue-green algae) are autotrophs and use CO_2 as a carbon source. They break down water into hydrogen and oxygen in presence of light energy	The process requires light energy. Carrier gas is needed to collect the evolved gas from the culture. Separation of oxygen and hydrogen is another limiting factor
Light fermentation	Phototrophic purple nonsulfur bacteria	These are heterotrophs and produce hydrogen using simple organic matter as a carbon source and light as an energy source under anaerobic conditions	Efficient light penetration and distribution in a highly turbid culture media is a major rate-limiting condition. The process can only use simple organic substrates
Dark fermentation	Nonphototrophic fermentative bacteria	Heterotrophs that produce hydrogen using complex organics as both carbon and energy sources under anaerobic conditions	The yield of hydrogen production is relatively low. Hydrogen partial pressure needs to be controlled at relatively low levels to enhance hydrogen yield

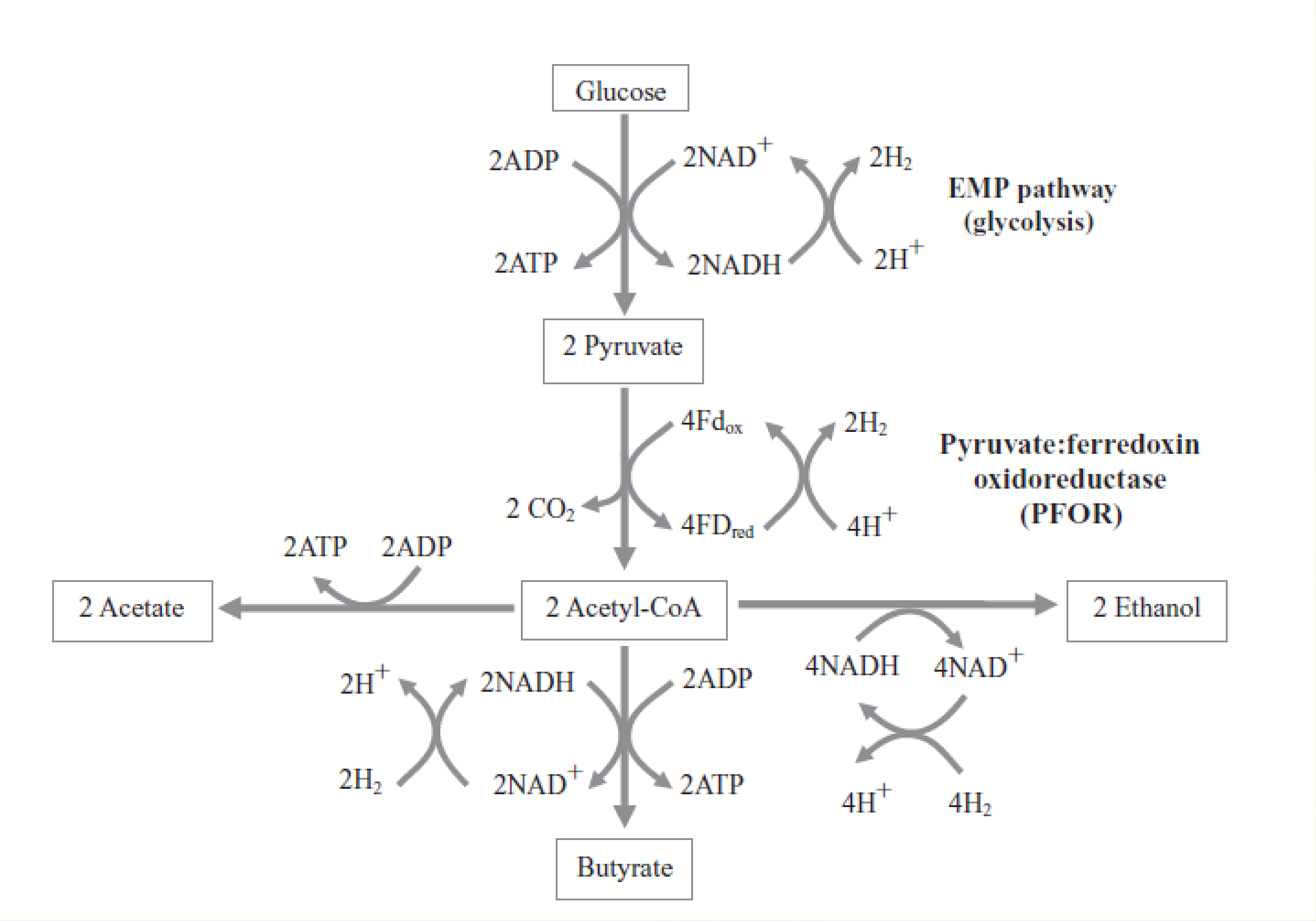
Thermodynamically, hydrogen production through photofermentation is not favorable unless light energy is supplied. In addition, only phototrophic bacteria are able to convert simple organic compounds such as organic acids to hydrogen, which thus limits the use of complex organic wastes. Dark fermentation continuously produces hydrogen from renewable sources such as carbohydrate-rich wastes without an input of external energy, a considerable advantage.

Hydrogen Production Pathway through Dark Fermentation

In most biological systems, hydrogen is produced by the anaerobic metabolism of
pyruvate formed during the catabolism of various organic substrates. Simple sugars
such as glucose are metabolized to pyruvate through various pathways that often
involve the Embden–Meyerhoff–Parnas (also known as glycolysis) and the Entner–Doudoroff pathways.



Hydrogen production pathway of enteric bacteria during dark fermentation.



Hydrogen production pathway of clostridia during dark fermentation.

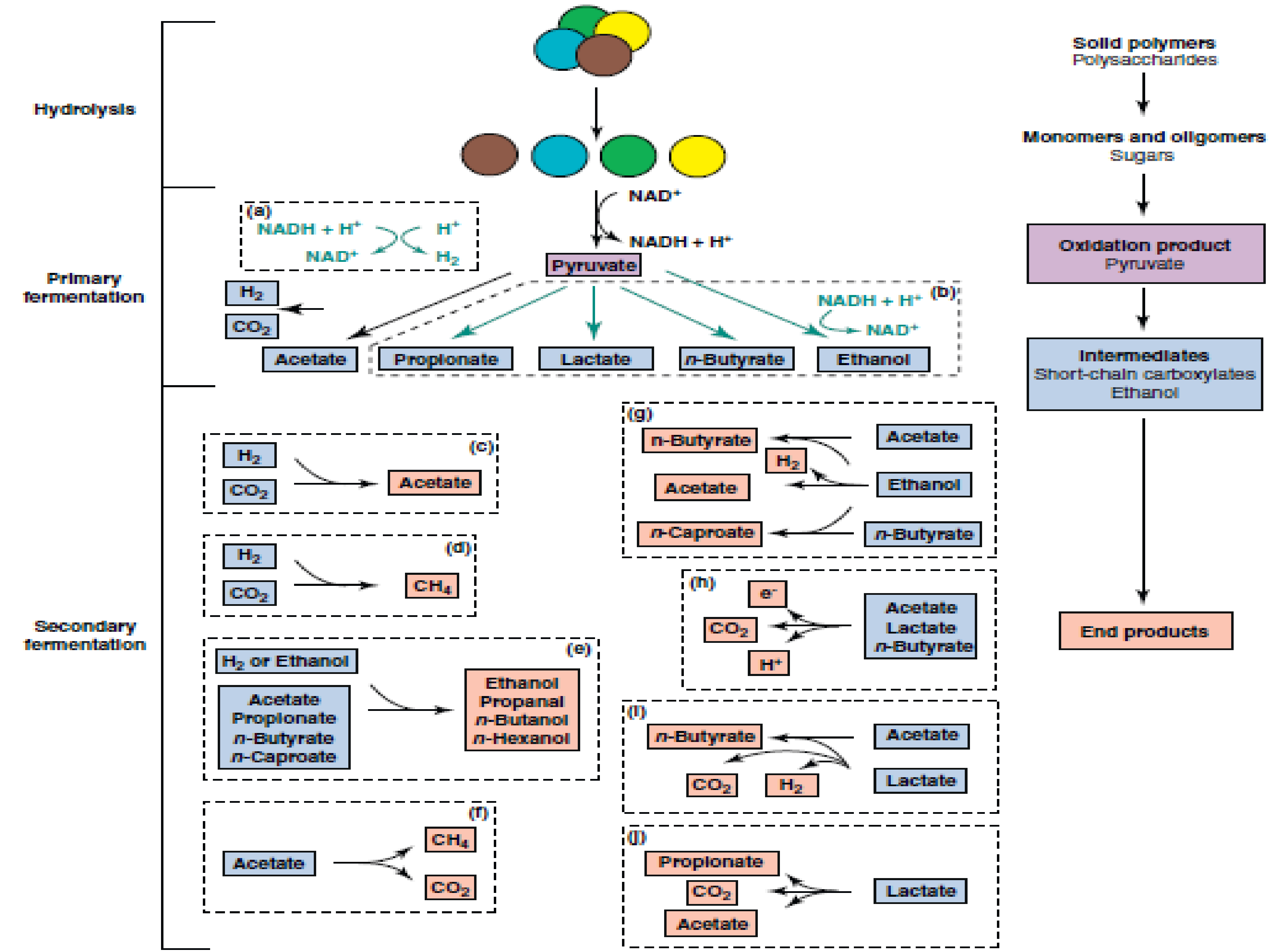
$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2, \quad \Delta G^\circ = -184\ \text{kJ} \quad \text{(enteric bacteria)}$$

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2, \quad \Delta G^\circ = -255\ \text{kJ} \quad \text{(clostridia)}$$

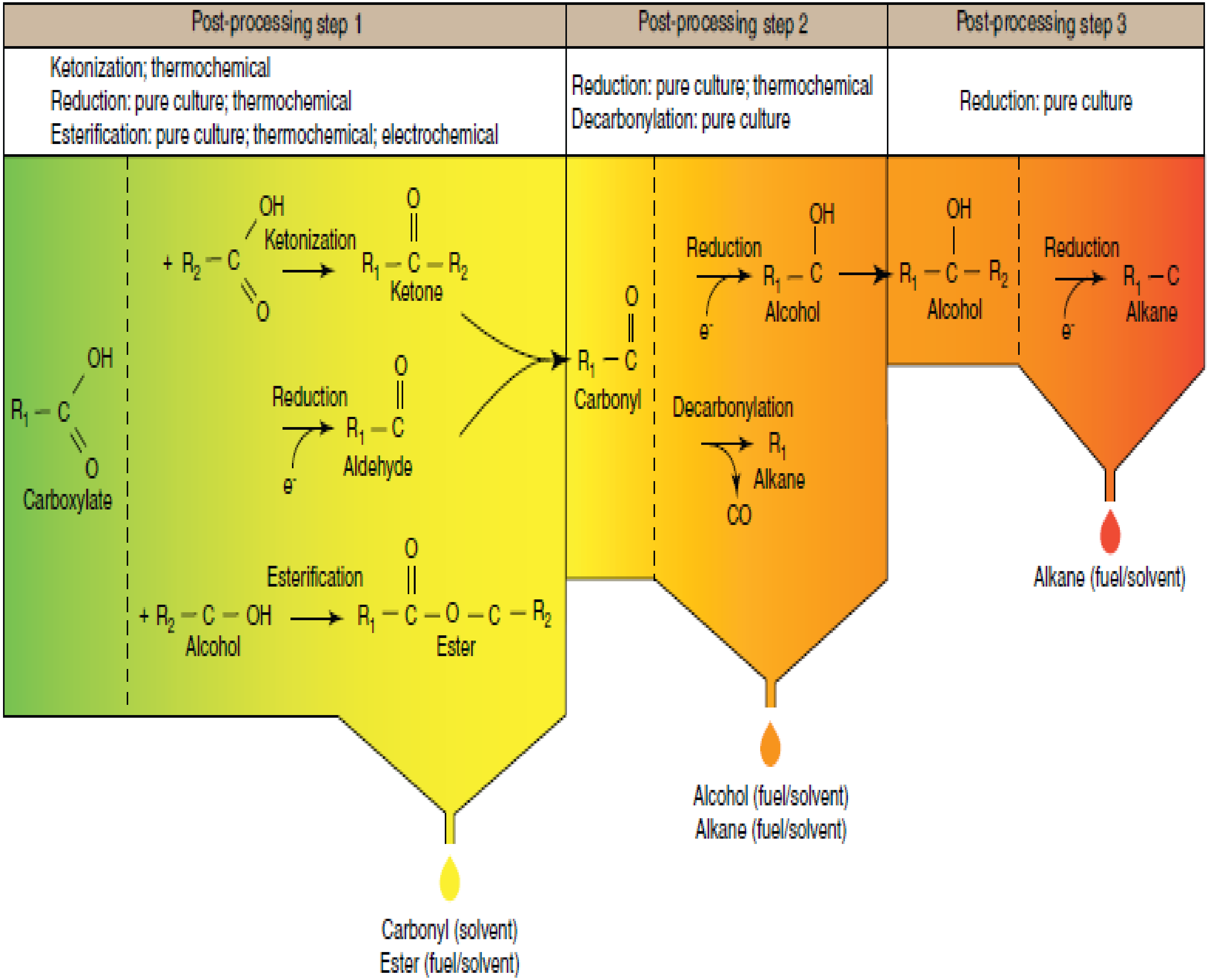
insoluble polysaccharides, such as cellulose and hemicellulose) and subsequent conversion by primary and fermentation reactions with undefined mixed cultures. During primary fermentation of sugars, substrates are converted to pyruvate, which results in the production of NADH and H+. All equivalents must be re-oxidized via H+ reduction by: (a) NADH oxidation; or (b) NADH oxidation via reduction of pyruvate or its oxidized organic derivatives, depending upon the hydrogen partial pressure.

At increasing hydrogen partial pressures, the flow of electrons from NADH shifts from H_2, acetate and CO_2 production towards formation of increasingly reduced fermentation products. CO_2 and H_2 are produced in the pyruvate oxidation reaction that is catalyzed by pyruvate: ferredoxin oxido reductase.

The products of primary fermentation can react further within undefined mixed cultures through several secondary fermentation reactions: (c) autotrophic homoacetogenesis; (d) hydrogenotrophic methanogenesis; (e) carboxylate reduction to alcohols with hydrogen or ethanol; (f) aceticlastic methanogenesis; (g) chain elongation of carboxylates with ethanol; (h) electricigenesis (i) lactate oxidation to n-butyrate (acetate and H+ as electron acceptor); and (j) lactate reduction to propionate (oxidation to acetate for energy conservation).

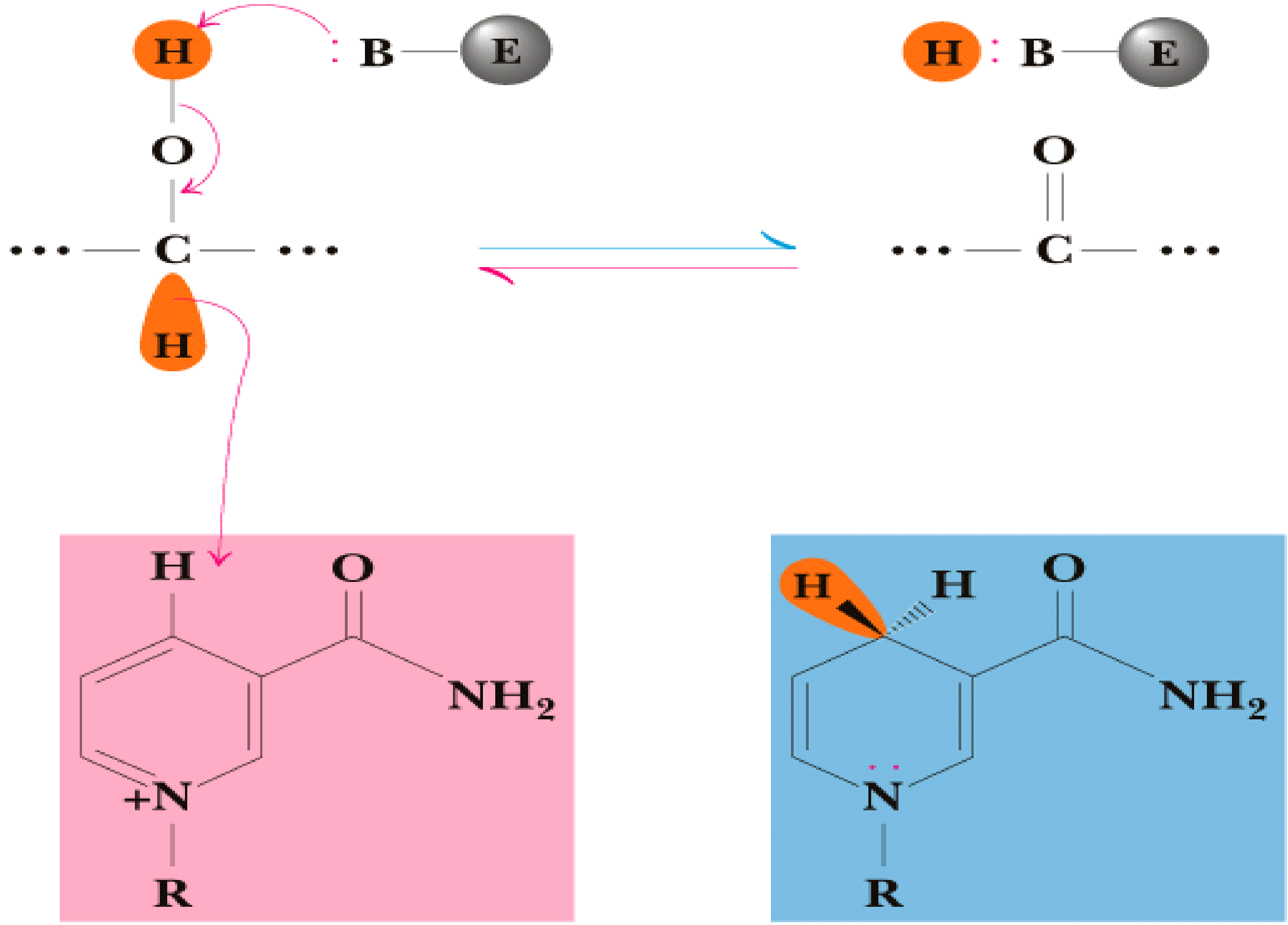


TRENDS in Biotechnology



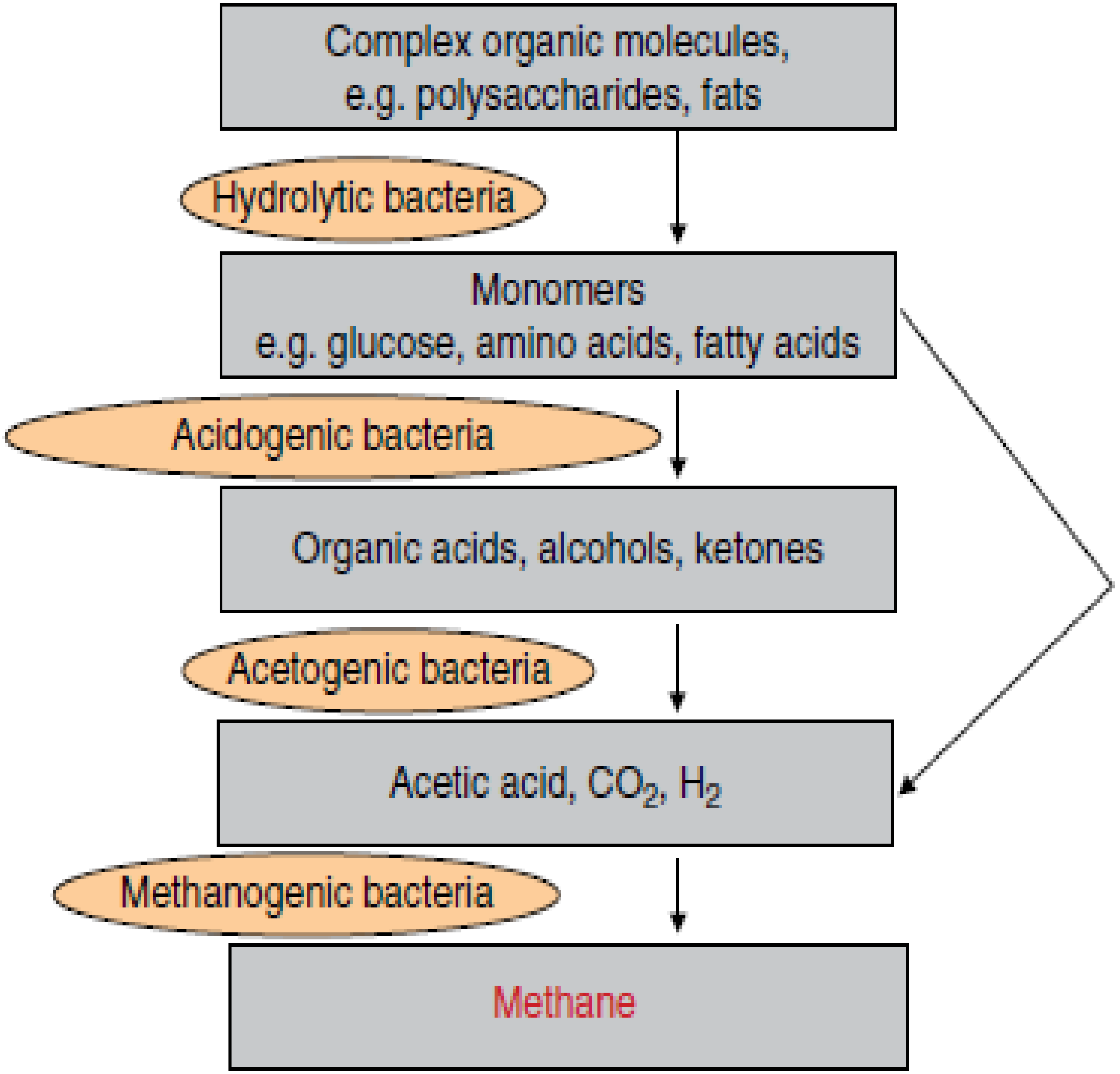
Post-processing step 1
Post-processing step 2
Post-processing step 3
Ketonization; thermochemical
Reduction: pure culture; thermochemical
Esterification: pure culture; thermochemical; electrochemical
Reduction: pure culture; thermochemical
Decarbonylation: pure culture
Reduction: pure culture
Carboxylate
Ketonization
Ketone
Reduction
Aldehyde
Esterification
Alcohol
Ester
Carbonyl
Reduction
Alcohol
Decarbonylation
Alkane
CO
Alcohol
Reduction
Alkane
Carbonyl (solvent)
Ester (fuel/solvent)
Alcohol (fuel/solvent)
Alkane (fuel/solvent)
Alkane (fuel/solvent)

Chemical post-processes that convert carboxylates to bulk fuels or solvents with pure-culture biochemical, electrochemical, and thermochemical steps, or a combination thereof. In post-processing step 1, carboxylates are converted to esters via esterification; are reduced to carbonyls; or ketonized to carbonyls. In post-processing step 2, the carbonyl intermediates are converted to alkanes via decarbonylation; or reduced to alcohols. Finally, in post-processing step 3, the alcohol intermediates are converted to alkanes via reduction. Other conversions are possible.



Oxidized coenzyme
(NAD^+ or $NADP^+$)

Reduced coenzyme
(NADH or NADPH)


Complex organic molecules,
e.g. polysaccharides, fats
Hydrolytic bacteria
Monomers
e.g. glucose, amino acids, fatty acids
Acidogenic bacteria
Organic acids, alcohols, ketones
Acetogenic bacteria
Acetic acid, CO_2, H_2
Methanogenic bacteria
Methane

Basic Ethanol Proces

Feed molasses ← Pretreatment (release of sugars)

↓

Hydrolysis (breakdown to fermentable sugars) ← Enzymer

↓

Fermentation → CO_2

↓

Feed (Vinasse Distillers grain) ← Destillation

↓

Ethanol